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Anthropogenic Pollution in İzmit Bay: Heavy Metal Concentrations in Surface Sediments

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Abstract

The extent of marine pollution in İzmit Bay is studied using geochemical data in surface sediments. The concentrations of 41 elements in 24 samples establish that surface sediments in inner and central İzmit Bay display significant enrichments in Ag, As, Cd, Cr, Co, Cu, Hg, Mo, P, Pb, Sb, Ti, V, and Zn associated with high concentrations of total organic carbon and sulphur. Geo-accumulation indices indicate that the inner and central İzmit Bay surface sediments are moderately to very strongly polluted with respect to Ag, Cd, Hg, Mo and Sb, and unpolluted to moderately polluted with respect to As, Co, Cu, Pb, and Zn. Despite total sedimentary concentrations above their pre-industrial background levels, geo-accumulation indices show that the surface sediments in İzmit Bay are unpolluted with respect to Cr, Ti and V. Except for a localized area offshore Tuzla, the outer İzmit Bay is generally unpolluted with respect to heavy metals.

Key Words: İzmit Bay, Marine Pollution, Heavy Metals

İzmit Körfezi'nde Oluşan Antropojenik Kirlilik: Yüzey sedimanlarındaki Ağır Metal Yoğunlukları

Özet

İzmit Körfezindeki deniz kirliliğinin boyutları yüzey sediman örneklerinde yapılan jeokimyasal çalışma sonucu incelenmiştir. Toplam 24 örnek üzerinde belirlenen 41 elementin analizleri sonucu , iç ve orta Körfez yüzey sedimanlarının toplam organik karbon ve sülfür ile gelişen Ag, As, Cd, Cr, Co, Cu, Hg, Mo, P, Pb, Sb, Ti, V, ve Zn gibi ağır metal yoğunluklarında önemli bir artış olduğu saptanmıştır. Yapılan jeo-akümülasyon hesaplamaları ise iç ve orta Körfezin Ag, Cd, Hg, Mo ve Sb yönünden kirli ve çok kirli, As, Co, Cu, Pb, and Zn yönünden ise az kirli olduğunu göstermektedir. Yine jeo-akümülasyon hesaplamaları sonucu, sedimandaki yoğunluklarının sanayi öncesi yoğunluklarından fazla bulunmasına karşın İzmit Körfezi sedimanlarının Cr, Ti ve V yönünden kirlenmediği saptanmıştır. Dış körfez ise, Tuzla bölgesinin bazı bölgeleri dışında ağır metal yönünden kirli değildir.

Anahtar Sözcükler: İzmit Körfezi, Deniz Kirliliği, Ağır Metaller

Introduction

İzmit Bay is a small east-west trending embayment situated along the northeastern Marmara Sea (Fig. 1). It is naturally divided into three physiographic regions: the inner bay, the central bay and the outer bay. The shallower (<20 m) inner bay is separated from the larger and deeper (<150 m) central bay by a 1.5 km-wide constriction between the town of Gölcük and İpraş Refinery (Fig. 2). The central bay is separated from the west-flaring and deepening outer bay through a 3 km-wide and ∼ 50 m deep constriction between Dil Burnu and Diliskelesi (Fig. 2).

Approximately 2 million people live around İzmit Bay, mainly in 3 large metropolitan centers, İzmit, Yalova and Tuzla, and several smaller single-industry towns, such as Darıca, Gölcük, Hereke, İpraş, and Karamürsel. İzmit Bay and its surroundings comprise one of the most heavily industrialized regions of northwestern Turkey, with large petrochemical and chemical plants in İzmit, İpraş and Yalova; civilian and military shipyards at Tuzla and Gölcük, respectively; heavy steel industries in İzmit; textile and related industries in Hereke and Karamürsel; leather tanning and processing plants in İzmit and Yalova, and automotive industries in İzmit. Over the last 100 years, the effluents from these industries have been draining into the coastal waters of İzmit Bay.

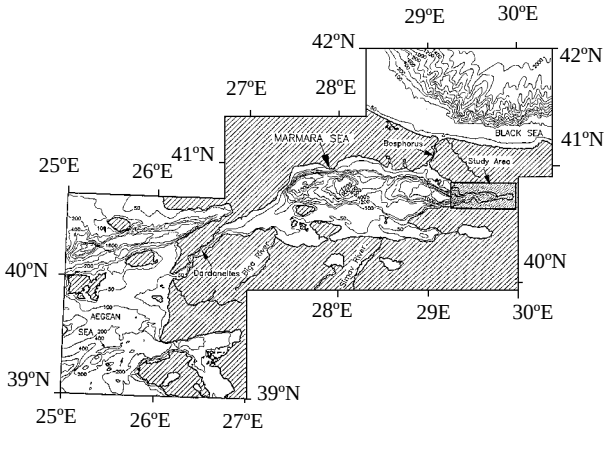

Figure 1. Map of the Marmara Sea and surroundings, showing İzmit Bay and the location of core MAR97-25. Isobaths are in metres.

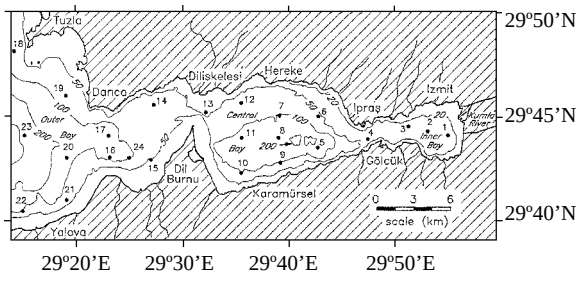

Figure 2. Bathymetry of İzmit Bay, showing the locations of the surface samples used in this study. Isobaths in metres.

During the last 20 years, a number of studies have been carried out on the effects of industrialization and urbanization in coastal marine sediments of the Marmara Sea, where the assessment of the anthropogenic pollution was made using the total concentrations of only a limited number of elements (Al, Cu Co, Cr, Fe, Mn, Ni, Pb, Zn) in surficial samples (e.g., Taymaz et al, 1983, Ergin et al., 1991). However, in these studies the total sedimentary concentrations of many heavy metals with high toxicity, such as As, Ag, Cd, Hg, Mo and Sb, have not been determined; therefore, the critical data for the full assessment of the marine environmental pollution in these embayments is limited at best. This paper present the results of the first comprehensive study examining the levels of pollution in İzmit Bay using a large array of inorganic elemental geochemical data from surface sediments.

Materials and Methods

Surface sediment samples were collected from 24 stations in İzmit Bay (Fig. 2) using a modified grab sampler during the 1995 cruise of the RV *KocaPiriReis* of the Institute of Marine Sciences and Technology, Dokuz Eylül University. All samples were kept in a deep-freezer until the end of the cruise; subsequently they were dried at 40°C. In 1997 a 200 cm-long gravity core (MAR97-25) was recovered from the eastern Marmara Sea at water depths of ∼1200 m to act as a site for background concentrations away from İzmit Bay (Fig. 1); this core was sub-sampled at 10 cm intervals, and all samples were also dried. Samples were shipped to Memorial University of Newfoundland for analysis.

A combination of X-ray fluorescence spectrometer (XRF), inductively coupled plasma emission spectrometer (ICP-ES) and atomic absorption spectrophotometer (AAS) was used to determine the to-

tal levels of the following elements in 24 surface and 19 core samples: Ag, Al, As, Ba, Be, Ca, Ce, Cd, Cl, Co, Cr, Cu, Dy, Fe, Ga, Hg, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, S, Sb, Sc, Si, Sr, Th, Ti, U, V, Y, Zn and Zr. Table 1 gives the full geochemical data from İzmit Bay surface samples and the MAR97-25 reference site, as well as the analytical detection limits for these elements. Total organic carbon was determined using the technique described in Aksu et al. (1995).

For major and trace element determinations using ICP-ES or AAS, except Ag, As, Cd, Hg, Rb and Sb, sediments were powdered and ∼5 g of powder was treated with 30% H_2O_2 to extract elements absorbed by organic matter and amorphous oxides. Samples were then digested in 15 ml of HF, 5 ml of concentrated HCl and 5 ml of 1:1 $HClO_4$ at 200°C and subsequently in 50 ml of 20% HCl at 100°C. Measurements were carried out using an ARL ICP-ES instrument. Samples for Cd analyses were processed as above and Cd was measured using a Varian Model AA1275 AAS. For the determination of Ag, samples were digested for 16 hours in 2 ml of concentrated HNO_3 at room temperature, and then for a further 2 hours in a hot water bath at 90°C. Determinations were made using AAS. For As and Sb determinations, samples (5 g each) were partially digested in concentrated HNO_3; subsequently, 1 ml of concentrated HCl was added and the samples were digested for a further 90 minutes. As and Sb were measured using ICP-ES. For Hg determinations samples (5 g each) were digested in 10 ml concentrated HNO_3 and 1 ml of concentrated HCl for 10 minutes. Samples were then placed in a hot water bath at 90°C and digested for an additional 2 hours. Hg was measured using ICP-ES; 4 on-peak and 4 off-peak measurements were made.

For XRF analyses, sediments were powdered and 4 g of powder was mixed with 0.7 g of phenolic resin binder. After homogenization, XRF pellets were prepared and baked for 15 minutes at 200°C. Elements were determined using an XRF ARL 8420+ sequential wavelength-dispersive spectrometer, with an Rh end-window X-ray tube and an LiF200 crystal, specially treated for enhanced heavy element sensitivity. For energies > 7.471 keV (20°-50° 2Θ), a scintillation detector was used with power settings at 75 kV and 40 mA. For energies < 6.398 keV (50°-150° 2Θ), a flow-proportional detector was used with power settings at 30 kV and 100 Ma (Longerich, 1993). Scan times were 4-6 seconds for the most abundant elements, 20 seconds for the trace elements and 100 seconds for Rb, Y and Nb. The intensities were then matrix-corrected by Compton correction for elements with emission energies greater than Fe, and by the LaChance-Traill algorithm (Longerich, 1993) for elements with emission energies less than and including Fe.

Results

Elemental associations

The inorganic geochemical data consist of measurements of 41 variables in 24 surface samples (Table 1). This large data set does not allow an immediate and unambiguous interpretation of elemental associations and potential sources in the sediments. Factor analysis was used to obtain simple patterns from this complex data set. The technique extracts a small number of hypothetical variables (R mode) or samples (Q mode), referred to as "factors", which account for a given percentage of the total variance in the data set. Both Q and R mode factor analyses were performed on the geochemical data from İzmit Bay.

Factor analysis results show that 3 factors account for a total of 96.5% of the total variance. The remaining 3.5% of the total variance not accounted for by the factor analysis is assumed to be random. Factor 1 accounts for 37.6% of the total variance and shows very high factor loadings in Al and Si, with statistically significant loadings (i.e. >0.3; Klovan and Imbrie, 1971) in Be, Ca, Dy, Fe, Ga, K, La, Li, Mg, Mn, Nb, Ni, Rb, and Y. This factor represents the aluminosilicates: the most common constituent of siliciclastic marine sediments. Factor 2 accounts for 35.9% of the total variance and shows very high loadings in C and S, but also shows significant loadings in Ag, As, Cd, Cr, Co, Cu, Hg, Mo, P, Pb, Sb, Ti, V, and Zn. This factor clearly represents the organic matter and the enrichments of those metals which are most commonly associated with high total organic carbon in marine sediments (e.g., Aksu et al., 1998). Factor 3 accounts for 23.0% of the total variance and shows high factor loadings in Ca and Mg, with significant loadings in Sr and Sc. This factor probably represents the carbonate (biogenic and detrital) in the study area.

Elemental background concentrations

The average shale values (Turekian and Wede-

pohl, 1961) commonly used for elemental background concentrations (e.g., Ergin et al., 1991) cannot account for the local variations in rock composition and chemistry in the Marmara Sea, and are unlikely to be representative of the İzmit Bay surface sediments. Instead, the background concentrations of the 40 elements used in this study were estimated in a ∼200 cm-long core (MAR97-25) recovered from the Eastern Marmara Basin, immediately west of İzmit Bay. Nineteen samples between 20 cm and 200 cm depth in MAR 97-25 were selected for the determination of elemental background concentrations. Radiometric dates in cores from the eastern Marmara Sea (e.g., Evans et al., 1989; Ergin et al., 1994) show that the rate of deposition in deep basins is ∼100 cm per 1000 years, suggesting that the sediments used for the calculation of elemental background concentrations were deposited between 2000 and 200 yrBP. Because this core site is far removed from the regions of immediate anthropogenic effluent input, and the sediments used in the calculations clearly pre-date the industrial period, the elemental concentrations in these samples must approximate the background levels in the eastern Marmara Sea. The background level of each element was calculated as the average value of that element in 19 samples in core MAR97-25, presented in Table 1.

Anthropogenic pollution in surface sediments

The level of anthropogenic pollution in İzmit Bay is evaluated using the technique described by Müller (1979), where the enrichment of an element above the background level (geo-accumulation index) is calculated using the following equation:

$$\text{Igeo} = \log_2 \text{ Cn / 1.5 x Bn}$$

where Igeo = index of geo-accumulation, Cn = measured concentration of the element in the muddy sediment being studied and Bn = geochemical background value (e.g., MAR97-25); the factor 1.5 is used to compensate for possible variations of the background data due to post-depositional changes (Müller, 1979). Igeo values were calculated for 40 elements (except C) in İzmit Bay surface sediments using the inorganic geochemical data (Cn) and the elemental background concentrations (Bn) from the deep Marmara Sea core MAR97-25. The data show that Ag, As, Cd, Cr, Co, Cu, Hg, Mo, P, Pb, Sb, Ti, V, and Zn, all associated with factor 2, consistently exhibit total sedimentary concentrations above their background levels in İzmit Bay surface sediments.

Enrichments in chalcophile (eg., Cu, As, Ni and Zn) and siderophile elements (eg., Cr, Ti and Fe) associated with sediments rich in total organic carbon and sulphur occur naturally in oxygen-deficient/anoxic basinal settings. In such environments, sulphate reduction takes place at the seafloor, as in the Black Sea (Landing and Lewis, 1991), or immediately below the sediment-water interface, as for the Aegean Sea sapropel S1 (Aksu et al., 1995), leading to the formation of highly insoluble sulphides in the presence of H_2S, and hence enrichments. However, many of the chalcophile and siderophile elements are also anthropogenic in origin. Thus, the distinction between natural and anthropogenic sources is often complicated. The occurrence on İzmit Bay surface sediments of the rarer but notorious environmental polluters Ag, Cd, Hg and Mo in quantities well above their background concentrations, and their clear associations and covariances with total organic carbon, P and S as well as the heavy metals As, Cu, Co, Cr, Pb, Sb, Ti, V and Zn (e.g., Aksu et al., 1998), strongly suggest that factor 2 truly represents anthropogenic pollution in the study area, rather than natural enrichment in poorly oxygenated sediments.

Distribution of TOC, S and heavy metals in surface sediments

Total organic carbon values are high in İzmit Bay surface sediments, ranging from 1.9-2.6% in the inner bay, to 2.0-3.0% in the central bay and 0.5-0.7% in the outer bay, except for 1.8% offshore of Tuzla (Fig. 3; Table 1). These total organic carbon values are slightly higher than the 0.5-1.7% calculated by Ergin et al. (1991) from İzmit Bay. Total sulphur concentrations show a similar trend to that of total organic carbon, with the highest values of 0.6-1.0% occurring in inner and central İzmit Bay, and show a notable decline in outer İzmit Bay (Fig. 3; Table 1). Total silver concentrations range between 0.1 and 0.7 ppm in İzmit Bay surface sediments, with moderately high values occurring mainly in the central bay, and the highest value recorded at station 18 offshore of Tuzla (Figs. 2, 4; Table 1). The background value of silver in core MAR97-25 is 0.08 ppm, which suggests that it is moderately enriched in inner and central bay surface sediments. Cadmium concentrations are high in central İzmit Bay (0.5-1.0 ppm) and moderate in the inner bay (0.4-0.6 ppm), but are generally low (<0.4) in the outer bay, except at station 18 (Fig. 4; Table 1). Cadmium is rare in uncontaminated deep Marmara Sea sediments (MAR97-25), ranging

Table 1. Elemental concentrations (μg/g = ppm) in İzmit Bay surface sediments. DL= detection limit in ppm. EBC= elemental background concentrations (in ppm) in eastern Marmara Sea, calculated as the average concentrations in 19 samples from core MAR97-25. < DL

	Ag	Al	As	Ba	Be	C	Ca	Cd	Ce	Cl	Co	Cr	Cu	Dy	Fe	Ga	Hg	K	La	Li
DL	0.03	30	2	1	0.1	—	18	0.05	1	25	0.1	1	1	0.1	18	1	0.05	18	1	0.1
EBC	0.08	75058	15	400	1.9	—	55772	0.1	74	18799	28	159	34	4.9	54809	19	0.07	21152	32	63
Station																				
1	0.2	87252	18	341	1.8	19407	38860	0.5	45	9188	56	236	77	3.4	61520	20	1.0	20301	24	59
2	0.1	99428	17	317	1.8	26009	36465	0.4	43	19324	49	130	59	3.5	60204	21	1.0	22476	22	56
3	0.2	77200	12	433	1.7	23985	16724	0.5	52	40403	42	143	61	3.8	58739	19	1.5	18386	26	47
4	0.2	77384	11	444	1.6	26130	30459	0.5	54	19955	45	406	52	2.9	41920	13	1.0	20069	27	51
5	0.1	78301	19	495	1.9	23238	45191	0.1	60	8898	35	271	37	3.3	42924	17	1.3	22202	29	48
6	0.4	56211	20	322	1.9	28418	34296	1.0	66	99480	47	150	49	4.3	55575	19	1.5	20128	39	62
7	0.4	46636	19	311	1.9	31182	36350	1.0	64	78608	60	215	46	5.5	59807	17	1.0	18994	44	66
8	0.3	49757	28	276	1.6	30762	35702	0.9	55	81648	18	150	43	3.5	55981	18	0.6	19020	30	53
9	0.3	50171	27	292	1.8	26165	33369	0.7	53	91633	20	144	45	3.3	57184	18	1.0	18769	28	58
10	0.2	56221	13	284	1.8	22902	42200	0.5	51	89910	18	127	41	3.2	53317	15	0.8	18420	27	57
11	0.2	69585	15	297	1.8	22909	32042	0.4	52	42335	19	123	39	3.5	54953	17	0.7	20455	29	60
12	0.3	48010	19	288	1.8	23458	39601	0.7	56	71403	17	134	38	3.8	54752	17	0.5	18825	32	57
13	0.2	60788	30	291	1.3	12051	61695	0.5	44	27197	22	225	47	2.5	44443	11	0.4	18160	24	38
14	0.1	58665	10	292	1.2	7101	97046	0.3	48	21240	26	282	26	2.9	36322	11	<DL	15994	25	38
15	0.2	64940	18	279	1.6	6024	41709	0.3	52	52382	35	164	41	3.3	53178	16	<DL	17770	26	53
16	0.3	77959	21	290	1.7	5178	47399	0.4	50	25344	18	137	39	3.1	52421	17	<DL	18848	27	51
17	0.1	63298	25	259	1.3	5001	95699	0.4	43	27657	15	110	25	2.8	40678	13	<DL	17328	27	40
18	0.7	70200	10	302	1.8	12014	99480	0.8	72	22925	11	132	82	3.6	38098	15	<DL	19662	40	36
19	0.1	49540	26	290	1.8	7124	53887	0.4	54	49484	17	135	38	3.3	54163	17	<DL	17525	29	56
20	0.2	78887	14	304	1.8	5146	47476	0.3	53	28585	19	148	39	3.1	54095	18	<DL	20180	28	55
21	0.2	44757	13	271	1.5	4190	42002	0.2	55	91947	31	144	38	3.0	55180	15	<DL	16249	28	52
22	0.1	74249	15	289	1.3	4056	45408	0.2	44	14237	27	199	26	2.8	44892	14	<DL	16086	24	41
23	0.1	55908	6	203	1.0	3814	88378	0.3	36	21521	18	205	20	2.1	34787	9	<DL	15888	22	33
24	0.3	51780	23	285	1.7	6234	43589	0.3	53	93550	18	129	37	3.0	55362	16	<DL	17522	28	54

Table 1. Continued

	Mg	Mn	Mo	Na	Nb	Ni	P	Pb	Rb	S	Sb	Sc	Si	Sr	Th	Ti	U	V	Y	Zn	Zr
DL	50	1	0.1	64	0.7	1	1	1	0.7	9.9	0.03	0.1	27.8	1	2.8	1	3.4	1	0.6	1	1.1
EBC	28350	3325	1.9	13568	14	87	409	27	119	4606	0.7	23	214626	250	8.5	4615	1.5	148	25	63	99
Station																					
1	24969	450	4.1	12254	11	66	600	32	95	8722	1.4	19	217210	134	6.5	5683	1.0	179	23	171	77
2	30329	558	4.8	16712	12	49	598	20	91	7072	1.5	19	224613	124	4.8	6327	<DL	176	23	110	91
3	20681	427	8.1	26722	12	39	498	27	94	9048	1.4	19	210118	154	2.6	5350	0.1	169	24	135	112
4	19517	411	6.2	19265	13	108	444	29	89	7707	0.9	12	277935	184	6.0	4302	2.5	122	21	107	72
5	17158	999	7.2	11707	15	78	355	22	106	8041	1.0	12	279826	226	8.1	4349	3.3	107	23	75	80
6	17089	421	8.1	99937	12	46	528	43	111	8375	1.8	16	172541	176	0.9	4872	0.8	185	31	159	77
7	13469	562	8.5	57014	13	65	762	42	111	6254	0.9	16	153599	173	4.9	4812	4.3	162	48	139	81
8	18337	893	8.9	60417	12	47	431	41	108	9415	0.8	14	159822	191	0.2	4467	1.2	184	22	158	72
9	14285	766	5.3	93073	12	47	406	43	109	6693	0.8	16	164914	172	2.0	4795	1.8	170	21	163	76
10	18792	591	4.6	75842	12	42	410	31	103	6398	0.8	15	179249	203	2.7	4647	2.1	159	19	147	78
11	24726	999	2.8	26367	12	43	448	35	108	7611	1.1	15	204464	154	2.0	4892	1.2	153	21	124	81
12	14501	435	3.8	52187	13	36	401	36	105	7143	1.8	15	159179	172	2.0	4699	1.5	150	24	133	80
13	17820	507	5.2	19641	10	58	619	43	77	4926	0.9	9	255901	231	3.2	3420	2.7	117	14	156	56
14	19481	450	2.7	20191	8	64	447	21	66	3878	0.6	9	238320	504	5.5	3343	0.1	90	15	79	52
15	19371	474	1.5	54330	12	51	453	26	90	3558	0.7	16	207449	180	5.1	5134	0.4	150	20	112	83
16	25806	500	<DL	18229	12	46	535	31	95	3607	0.9	15	232452	197	3.3	5186	1.9	153	20	114	73
17	20650	427	<DL	23715	10	24	525	30	78	2843	0.7	10	232238	313	5.1	3943	2.4	105	17	99	54
18	15467	228	3.3	16539	21	25	658	61	102	7417	0.8	10	221406	403	10.5	5088	3.0	116	25	240	78
19	15087	438	<DL	36683	14	37	419	39	102	2683	1.1	15	167256	218	5.5	4714	1.0	134	20	25	76
20	28436	622	<DL	18077	13	58	521	36	106	3026	1.1	15	228587	212	4.5	4924	1.2	152	19	117	69
21	12187	468	1.8	90166	12	45	348	28	89	2137	1.1	15	162113	182	2.9	5141	1.6	153	20	98	72
22	22033	525	<DL	16169	10	44	492	27	70	2214	0.9	13	259116	181	7.6	4963	0.6	128	18	82	70
23	21065	342	1.1	14767	8	44	388	21	62	2785	1.0	8	234571	233	3.4	3249	0.4	91	13	59	36
24	14757	514	<DL	87348	13	36	404	28	96	2219	1.3	16	176525	184	5.0	5061	0.4	145	29	112	76

Table 1. Continued

	Mg	Mn	Mo	Na	Nb	Ni	P	Pb	Rb	S	Sb	Sc	Si	Sr	Th	Ti	U	V	Y	Zn	Zr
DL	50	1	0.1	64	0.7	1	1	1	0.7	9.9	0.03	0.1	27.8	1	2.8	1	3.4	1	0.6	1	1.1
EBC	28350	3325	1.9	13568	14	87	409	27	119	4606	0.7	23	214626	250	8.5	4615	1.5	148	25	63	99
Station																					
1	24969	450	4.1	12254	11	66	600	32	95	8722	1.4	19	217210	134	6.5	5683	1.0	179	23	171	77
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3	20681	427	8.1	26722	12	39	498	27	94	9048	1.4	19	210118	154	2.6	5350	0.1	169	24	135	112
4	19517	411	6.2	19265	13	108	444	29	89	7707	0.9	12	277935	184	6.0	4302	2.5	122	21	107	72
5	17158	999	7.2	11707	15	78	355	22	106	8041	1.0	12	279826	226	8.1	4349	3.3	107	23	75	80
6	17089	421	8.1	99937	12	46	528	43	111	8375	1.8	16	172541	176	0.9	4872	0.8	185	31	159	77
7	13469	562	8.5	57014	13	65	762	42	111	6254	0.9	16	153599	173	4.9	4812	4.3	162	48	139	81
8	18337	893	8.9	60417	12	47	431	41	108	9415	0.8	14	159822	191	0.2	4467	1.2	184	22	158	72
9	14285	766	5.3	93073	12	47	406	43	109	6693	0.8	16	164914	172	2.0	4795	1.8	170	21	163	76
10	18792	591	4.6	75842	12	42	410	31	103	6398	0.8	15	179249	203	2.7	4647	2.1	159	19	147	78
11	24726	999	2.8	26367	12	43	448	35	108	7611	1.1	15	204464	154	2.0	4892	1.2	153	21	124	81
12	14501	435	3.8	52187	13	36	401	36	105	7143	1.8	15	159179	172	2.0	4699	1.5	150	24	133	80
13	17820	507	5.2	19641	10	58	619	43	77	4926	0.9	9	255901	231	3.2	3420	2.7	117	14	156	56
14	19481	450	2.7	20191	8	64	447	21	66	3878	0.6	9	238320	504	5.5	3343	0.1	90	15	79	52
15	19371	474	1.5	54330	12	51	453	26	90	3558	0.7	16	207449	180	5.1	5134	0.4	150	20	112	83
16	25806	500	<DL	18229	12	46	535	31	95	3607	0.9	15	232452	197	3.3	5186	1.9	153	20	114	73
17	20650	427	<DL	23715	10	24	525	30	78	2843	0.7	10	232238	313	5.1	3943	2.4	105	17	99	54
18	15467	228	3.3	16539	21	25	658	61	102	7417	0.8	10	221406	403	10.5	5088	3.0	116	25	240	78
19	15087	438	<DL	36683	14	37	419	39	102	2683	1.1	15	167256	218	5.5	4714	1.0	134	20	25	76
20	28436	622	<DL	18077	13	58	521	36	106	3026	1.1	15	228587	212	4.5	4924	1.2	152	19	117	69
21	12187	468	1.8	90166	12	45	348	28	89	2137	1.1	15	162113	182	2.9	5141	1.6	153	20	98	72
22	22033	525	<DL	16169	10	44	492	27	70	2214	0.9	13	259116	181	7.6	4963	0.6	128	18	82	70
23	21065	342	1.1	14767	8	44	388	21	62	2785	1.0	8	234571	233	3.4	3249	0.4	91	13	59	36
24	14757	514	<DL	87348	13	36	404	28	96	2219	1.3	16	176525	184	5.0	5061	0.4	145	29	112	76

between its detection limit and 0.2 ppm, with an average concentration of 0.1 ppm (Table 1). These data suggest that the central and inner bay surface sediments are considerably enriched in cadmium. Cobalt values are generally low (10-25 ppm) in outer and central İzmit Bay, but notably increase to 40-60 ppm in the northeastern outer bay and the inner bay (Fig. 5; Table 1). The background level of this metal in the deep Marmara Sea core is 28 ppm, which indicates that only surface sediments from the inner and northeastern segment of the central İzmit Bay are slightly enriched in cobalt. Copper values are moderate in the study area, with the highest values occurring in inner İzmit Bay surface sediments and at station 18 offshore of Tuzla (Fig. 5). Its abundance in the uncontaminated Marmara Sea sediments ranges between 22 and 59 ppm, with an average of 34 ppm (Table 1), which is nearly identical to the average copper concentration of 35 ppm in shales (Adriano, 1986). These data show that copper is only slightly enriched in central and inner İzmit Bay sediments (Fig. 5; Table 1).

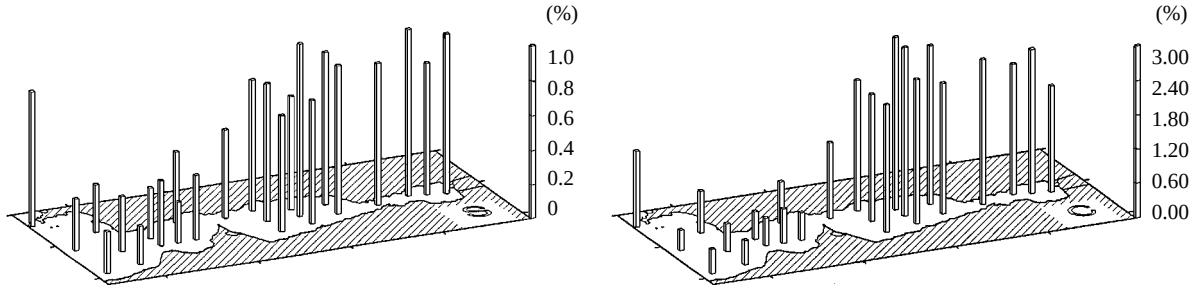


Figure 3. Bar graphs showing the distribution and abundance (%) of total sulphur (top) and total organic carbon (bottom) in İzmit Bay surface sediments.

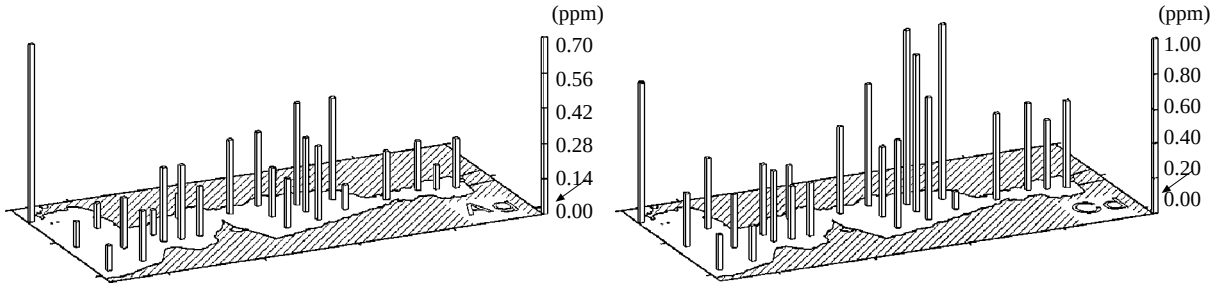


Figure 4. Bar graphs showing the distribution and abundance (ppm) of total concentrations of silver (top) and cadmium (bottom) in İzmit Bay surface sediments. Arrows indicate background concentrations.

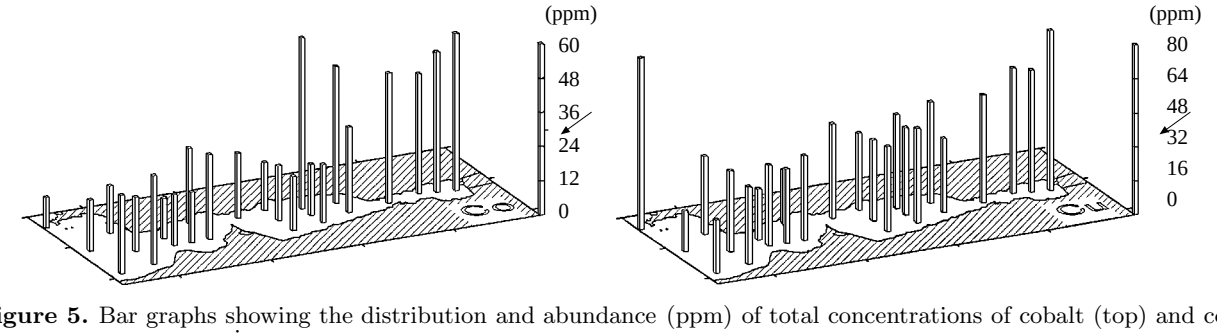


Figure 5. Bar graphs showing the distribution and abundance (ppm) of total concentrations of cobalt (top) and copper (bottom) in İzmit Bay surface sediments. Arrows indicate background concentrations.

Mercury concentrations are highest (1.2-1.5 ppm) in inner and eastern central İzmit Bay surface sediments and show a dramatic decline to 0.5 ppm at the Dil Burnu Entrance (Fig. 2), west of which the Hg values are below the detection limit in all samples (Fig. 6; Table 1). The background level of mer-

cury in Marmara Sea core MAR97-25 is calculated to be 0.07 ppm, which indicates that all samples from the inner and central İzmit Bay are considerably enriched in mercury. The distribution of molybdenum concentrations in surface sediments is similar to that of mercury, with the highest values of 7.0-9.0 ppm occurring in inner and central İzmit Bay (Fig. 6). West of the Dil Burnu Entrance, Mo concentrations are generally less than 3 ppm; for 6 samples values were below the detection limit. The pre-industrial background level of 1.9 ppm for this metal in core MAR97-25 shows that it is enriched by 5-7 ppm in the inner and central İzmit Bay surface sediments (Table 1).

Nickel concentrations range between 30 and 110 ppm in İzmit Bay surface sediments, with the highest values occurring in the eastern central bay and the entrance to the inner bay (Table 1). Ergin et al. (1991) reports nickel values ∼15-20% higher than those in this study. The background level for nickel is 87 ppm in the Marmara Sea core MAR97-25 (Table 1), so that except for one sample (station 4) none of the surface sediments in İzmit Bay show enrichment in nickel. Lead concentrations range between 21 and 61 ppm in İzmit Bay, with the highest values occurring in the central bay (30-50 ppm) and at station 18, offshore of Tuzla (Fig. 7; Table 1). These values are nearly identical to previously reported lead values from İzmit Bay (Ergin et al., 1991). A background level of 27 ppm suggests that the surface sediments throughout the study area are slightly enriched in lead.

Arsenic concentrations range between 6 and 30 ppm in İzmit Bay surface sediments (Fig. 7; Table 1). The background level of 15 ppm suggests that sediments from the inner, central and eastern segments of outer İzmit Bay are moderately enriched in arsenic. Antimony concentrations are variable but high in the study area, ranging between 0.5 and 1.8 ppm, with the highest values occurring in the inner bay and along the northern shores of the central bay (Fig. 8). Antimony is rare in the uncontaminated Marmara Sea sediments (Table 1), with an average value of 0.7 ppm in core MAR97-25. This indicates that most of the inner and central bay surface sediments are moderately enriched in this metal (Table 1). Zinc values are moderate in İzmit Bay with slightly higher values in the central bay, and the highest value at station 18 (Fig. 8; Table 1). Ergin et al. (1991) reported zinc values 40-50% lower than in this study.

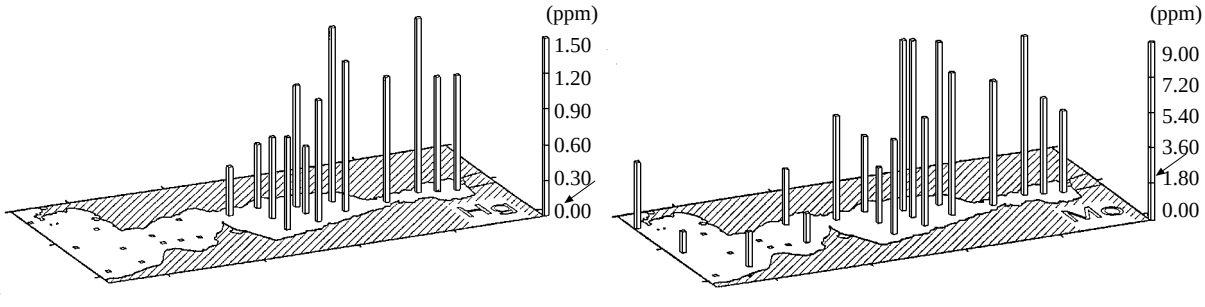


Figure 6. Bar graphs showing the distribution and abundance (ppm) of total concentrations of mercury (top) and molybdenum (bottom) in İzmit Bay surface sediments. Arrows indicate background concentrations.

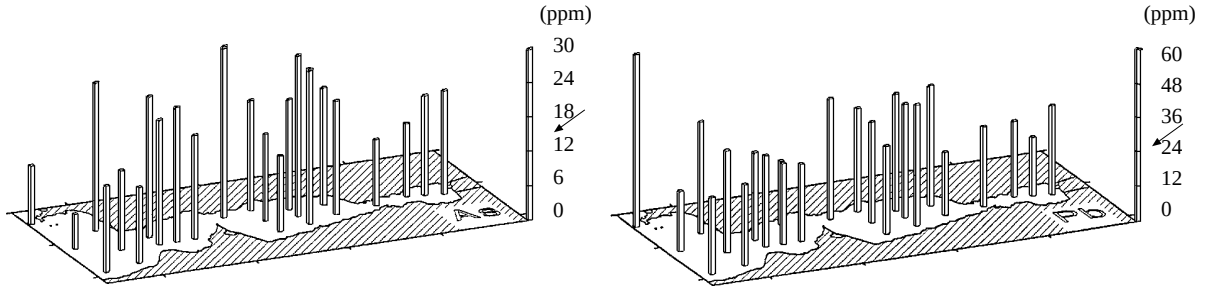


Figure 7. Bar graphs showing the distribution and abundance (ppm) of total concentrations of arsenic (top) and lead (bottom) in İzmit Bay surface sediments. Arrows indicate background concentrations.

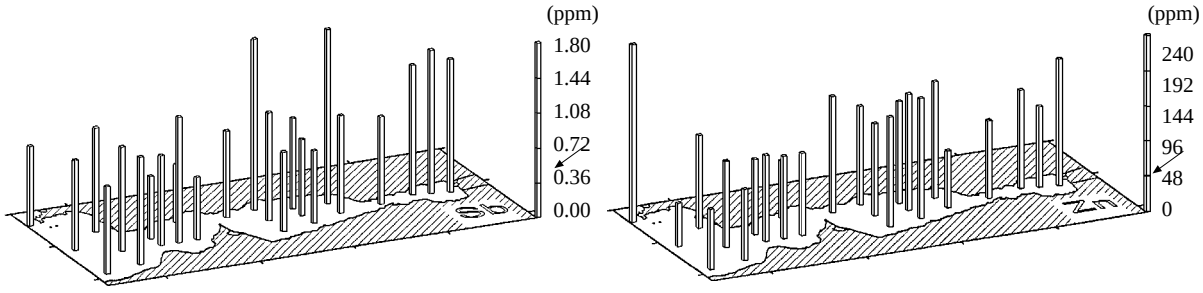


Figure 8. Bar graphs showing the distribution and abundance (ppm) of total concentrations of antimony (top) and zinc (bottom) in İzmit Bay surface sediments. Arrows indicate background concentrations.

Degree of sediment contamination

Figure 9 shows the geographical distribution of the normalized varimax components of factor 2 in İzmit Bay, where zones A to F correspond respectively to factor loadings of <0.15, 0.15-0.30, 0.30-0.45, 0.45-0.60, 0.60-0.75 and >0.75. The highest concentrations of heavy metals associated with factor 2 occur in inner İzmit Bay (Zone F), east of the İpraş-Gölcük line (Fig.9). The geo-accumulation indices show that this zone is strongly to very strongly polluted in Hg (2^5x1.5=48-fold enrichments; Igeo=5), strongly polluted in Cd (2^4x1.5=24-fold enrichments; Igeo=4), and moderately polluted in Ag, Mo and Sb (2^3x1.5=6-fold enrichments; Igeo=3). However, the zone is either unpolluted (Igeo=0) or unpolluted to moderately polluted with respect to As, Cr, Co, Cu, P, Pb, Ti, V and Zn, despite the fact that these elements display concentrations above their background levels (Fig. 9).

Zone E is located along the northeast segment of central İzmit Bay and displays strong to very strong pollution in Cd and Hg (Igeo=5), moderate to strong pollution in Ag (Igeo=3) and moderate pollution in Mo and Sb (Igeo=2; Fig. 9). A trend of decreasing Igeo values is clearly visible across central İzmit bay towards the outer bay (Zones D through A). Zone D extends from Diliskelesi to Hereke along the northern shores of central İzmit Bay, encircling Zone E, and in the northwestern portion of the study area offshore Tuzla (Fig. 9). It shows strong to very strong pollution in Cd (Igeo=5), strong pollution in Hg (Igeo=4), moderate to strong pollution in Ag (Igeo=3) and moderate pollution in Mo (Igeo=2). Zone C forms a narrow band at the western margin of Zone D in central İzmit Bay and encircles the small zone offshore of Tuzla. The zone displays strong pollution in Cd (Igeo=4), moderate to strong pollution in Hg (Igeo=3) and moderate pollution in Ag (Igeo=2; Fig. 9). Zone B mainly occurs in shallower shelf depths of outer İzmit Bay, as well as the southwestern segment of the central bay. These sediments are largely unpolluted except for moderate to strong pollution in Cd (Igeo=3), and moderate pollution in Ag and Sb (Igeo=2; Fig. 9). Zone A is situated along the deeper axis of outer İzmit Bay and shows only moderate pollution in Cd and Sb (Igeo=2; Fig. 9). Despite notable total sedimentary concentrations of Cr, Ti and V, the geo-accumulation index shows that surface sediments in İzmit Bay are unpolluted (Igeo=0) with respect to these elements. Similarly, these sediments are unpolluted to moderately polluted (Igeo=1) with respect to As, Co, Cu, P, Pb and Zn.

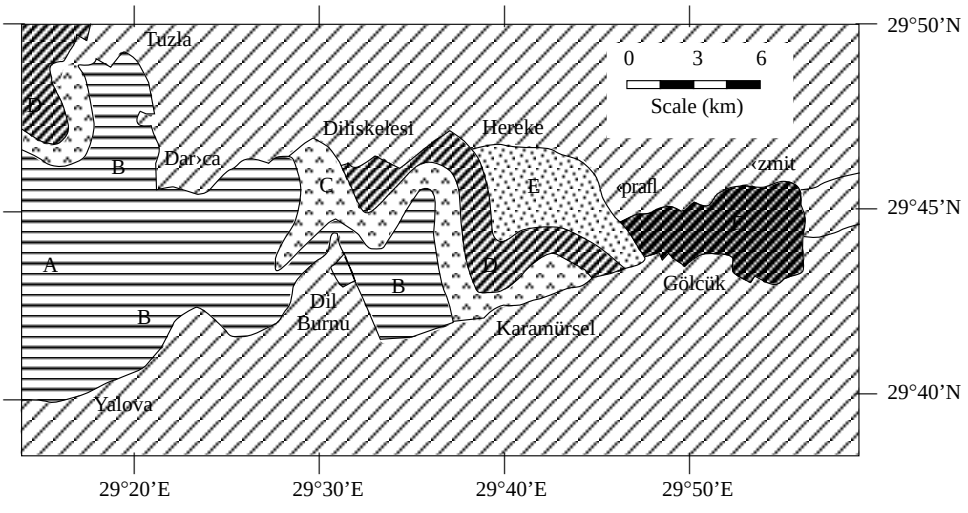
Discussion

The following general sources can be identified for the pollution observed in the İzmit Bay surface sediments:

1) Domestic pollution: untreated liquid and solid waste produced by the inhabitants of the cities, supplied to the bay by the sewage network and small creeks;

2) Industrial pollution: untreated liquid and solid waste produced by over 120 industrial centres, also supplied to the bay by the sewage network and small creeks;

3) Atmospheric pollution: particulate emission produced by vehicles, trains and vessels; fly ash emission from coal- and fuel-oil-burning plants, by-products of open-air burning of municipal and industrial solid waste and garbage, all of which are eventually transported into the inner and central Izmir Bay by precipitation and drainage.



POLLUTION INTENSITY	I_{geo}	I_{geo} class	POLLUTERS					
			A	B	C	D	E	F
very strongly polluted	>6	6						
strongly to very strongly polluted	>4-5	5				Cd	Cd Hg	Hg
strongly polluted	>3-4	4			Cd	Hg		Cd
moderately to strongly polluted	>2-3	3	Cd	Cd	Hg	Ag	Ag	
moderately polluted	>1-2	2	Sb	Ag Sb	Ag	Mo	Mo Sb	Ag Mo Sb
unpolluted to moderately polluted	>0-1	1	Ag As Cu	Mo Pb Zn	As Mo Pb Sb Zn	As Pb Sb Zn	Co P Pb Zn	Co Cu Zn
unpolluted	<0	0	Co Cr Hg Mo P Pb Ti V Zn	As Cu Co Hg Cr P Ti V	Cu Co Cr Ti V P	Cu Co Cr Ti V P	As Cr Cu Ti V	As Cr P Pb Ti V

Figure 9. Map of the study area showing the degree of sediment contamination by Ag, As, Cd, Co, Cu, Hg, Mo, Pb, Sb and Zn, discussed in text (top) and the index of geo-accumulation, Igeo (bottom) in İzmit Bay surface sediments.

There are numerous raw sewage outlets in the periphery of İzmit Bay, actively discharging ∼370,000 m^3 day^{-1} of waste water into the bay, including untreated sewage (TÇV, 1998). Approximately ∼51.4% (190,000 m^3 day^{-1}) of this discharge is domestic waste, 79% of which is discharged along the northern shores of İzmit Bay. Nearly all industrial waste is also untreated and is either discharged through the domestic sewage network or via a few small rivers and creeks. There are no data on the chemical composition of the sewage discharge into İzmit Bay. However, high total organic carbon in the surface sediments can be correlated with the organic waste input into the bay. For example, there are reports of periods of an intense foul smell emanating from the inner bay, particularly during the hot summer months. During these months, the dissolved oxygen levels in inner İzmit Bay decrease dramatically to values close to zero (TÇV, 1998), reflecting partial decomposition of organic waste in shallow waters, and suggesting that the bottom waters in this region must periodically become anoxic. Similar foul odours are reported along the shoreline seaward of the major sewage outfalls of smaller communities and industrial centres, particularly along the northern shores of the bay.

The high concentrations of total organic carbon in surface sediments (Fig. 3) reflect organic matter influx via effluent input, as well as input through the relatively high primary productivity in the water column (10-170 g C m^2 $year^{-1}$; TÇV, 1998). High phosphorus may be related to the use of detergents and the discharge of phosphate through the sewage system, particularly in central İzmit Bay (Table 1). Fly

ash from coal- and petroleum-burning plants, as well as the İpraş Refinery, is probably the major source of sulphur in İzmit Bay surface sediments (Fig. 3). Oxidation of the organic waste probably accounts for the low dissolved oxygen levels observed within the entire İzmit Bay water column.

There are over 120 major industrial centres along İzmit Bay, largely concentrated along the northern shores (Fig. 10). Many of these industries empty their untreated effluent into İzmit Bay; however, there are no data available on the types and rates of heavy metal discharges from these industries. Fifteen major industries discharge their waste waters into the inner bay, including 3 large pulp mills and chlor-alkali plants, 4 pharmaceutical and chemical plants, 4 petrochemical plants, 3 steel factories/smelters, and a leather factory (TÇV, 1998). SEKA (Fig. 10) is the largest of the pulp mills/chlor-alkali plants and provides over 50% of the anthropogenic organic matter influx into İzmit Bay (TÇV, 1998). A major proportion of the industrial effluent is supplied into the inner İzmit Bay via the Kumla River and its tributaries, including the discharges from a large slaughter house, a number of leather-processing plants and small smelters. Central İzmit Bay receives the effluent from 10 large industrial centres, including 4 chemical plants, 2 petroleum refineries, a chlor-alkali plant, a paper mill, a ceramic factory and two large textile factories (Fig. 10). Except for one large textile factory in Karamürsel, all these industries are concentrated along the northern shores of central İzmit Bay (Fig. 10). Three major industries discharge their waste into the outer bay, including a chemical plant, an automobile plant, and an appliance factory.

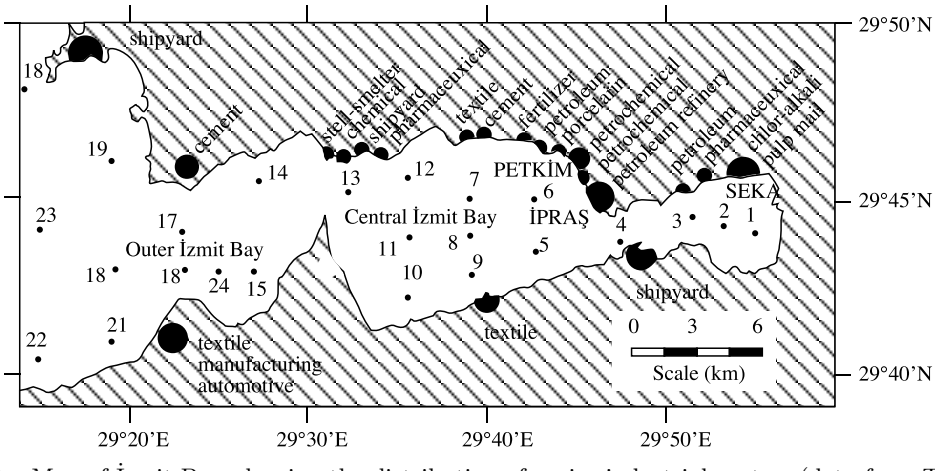


Figure 10. Map of İzmit Bay, showing the distribution of major industrial centres (data from TÇV, 1998).

Fly ash constitutes a major pollutant from coal-burning and is known to contribute notable quantities of As, Cd, Cu, Mo, Pb, Sb, and Zn to the environment (Natusch et al., 1975). Nearly all the smelters in the region use coal as their primary fuel. The fly ash emanating from these plants initially settles over the greater city of İzmit and it is probably quickly washed by rain into the inner bay via the sewage network and the Kumla River. Leather tanning plants which employ large quantities of arsenic and chromium salts in the tanning procedure discharge their untreated waste products directly into inner İzmit Bay. Nearly all antifouling paints applied to commercial, naval and recreational vessels at the large military shipyard at Gölcük and the civilian shipyards and docks at Tuzla and Dil Iskelesi (Fig. 2) contain significant quantities of copper and lesser quantities of antimony, lead and mercury, probably contributing the high total sedimentary concentrations of these heavy metals in inner İzmit Bay as well as offshore of Tuzla (Figs. 5-8).

The main source of lead in the study area is probably automobile traffic. Until recently, the great majority of the cars in Turkey had no catalytic converters and burned leaded petrol. Lead sulphide ore has also been used since antiquity for the extraction of silver impurities (Patterson, 1971). The effluent from large chlor-alkali plants as well as industries which use bleach probably supply most of the mercury and mercury salts found in the İzmit Bay surface sediments. The correlation between the highest mercury values in inner İzmit Bay and the SEKA complex

is noteworthy (Fig. 10). Until recently, mercury-bearing compounds have been used in the prevention and control of industrial slime, and these compounds eventually ended up in inner İzmit Bay. Large battery recycling plants are known for their potential for delivering mercury and lead compounds into the environment. Therefore, some mercury compounds are probably also supplied by the Kumla River. In the process of chromium- and nickel-plating and galvanizing, the surfaces to be plated are often cleaned using strong acids. This process leaches a number of heavy metals, which are released into İzmit Bay via the sewage network. Furthermore, various chromium, nickel and zinc pigments and compounds are used in metal plating, probably contributing some undeterminable quantities of these heavy metals into the bay via the Kumla River.

In the greater İzmit Bay region, cadmium is extensively used by various industries in the production of copper, lead, silver and aluminium alloys, and in various pigments. Some of the finest Turkish rugs are woven in Hereke, where cadmium, antimony, copper, cobalt and zinc salts are commonly used in the process of wool-dyeing. Cadmium salts are also widely used by the ceramic industries, and may also be contributed as wastes from zinc, lead and copper smelters. High cadmium abundances in central İzmit Bay, particularly along the northern shore (Fig. 4), appear to reflect the contributions from mainly the large ceramic plants and textile industries (Fig. 10). Silver in İzmit Bay surface sediments is probably largely supplied by photographic industries, with lesser contributions from the disposal of silver-zinc and silver-cadmium batteries.

Molybdenum is frequently found in municipal sludges at levels that are above the background concentrations (Adriano, 1986). In industrial regions it is mainly supplied by fly ash resulting from power generation using coal combustion, with estimates of 15 tonnes of Mo per year for every 1000 MW of power generated (Adriano, 1986). Molybdenum salts are also commonly used in fertilizers. The highest Mo concentrations in inner and central İzmit Bay, well above background levels, clearly suggest an industrial anthropogenic influx (Figs. 6, 10). The primary sources of vanadium in the study area are probably combustion byproducts of coal-burning plants and the fly ash from petroleum-fired plants in the form of vanadium pentoxide. Antimony is used in paints, lacquers, ceramic enamels and glass and pottery industries. It is also commonly used, alloyed with lead, by manufacturing industries. The notable abundance of antimony in the inner and central İzmit Bay surface sediments, above background levels, suggests contamination mainly from shipyards, and ceramic factories.

Ergin et al. (1991) concluded that the surface sediments in İzmit Bay are basically uncontaminated by anthropogenic pollution. This study was primarily based on the evaluation of the total sedimentary concentrations of a limited number of heavy metals: Cu, Co, Cr, Fe, Mn, Ni, Pb and Zn. The inorganic geochemical data presented in this paper strongly contradicts the conclusions of Ergin et al. (1991) and clearly show that the surface sediments in İzmit Bay are moderately to very strongly polluted with respect to Ag, Cd, Hg, Mo and Sb, with Igeo values between 2 and 5, and unpolluted to moderately polluted with respect to As, Co, Cu, Pb, and Zn, with Igeo values between 0 and 1. These data indicate that anthropogenic pollution must be viewed seriously within this embayment. The heaviest contamination is observed along the northeastern segment of the central bay offshore of Hereke and İpraş (Zone E) and the entire inner bay (Zone F; Fig. 9), reflecting the high concentrations of chemical, petroleum, chlor-alkali and pharmaceutical industries (Fig. 10). The data conclusively show that the anthropogenic pollution observed in inner and central İzmit Bay is almost exclusively confined to these regions by the shallow sill at the Dil Burnu Entrance (Fig. 9). The low tidal range and restricted water circulation between the central and outer parts of İzmit Bay control this confinement.

Most previous studies along the coastal waters of Turkey focussed on the surficial sedimentary concentrations of only a limited numbers of elements; thus, the distinction between the natural and anthropogenic elemental associations was not always possible (e.g., Ergin et al., 1991). In many instances, the sedimentary concentration of an element is assumed to be anthropogenic, because of the involvement of that element in polluted sediments elsewhere. The present study highlights the importance of a broader elemental data set in the assessment of anthropogenic pollution in small coastal embayments.

Increased concentrations of heavy metals in marine sediments enhance the importance of sediments as a direct source of potential toxins in nearshore environments. However, sediments geochemistry data, such as those presented here, provide no ev-

idence for biological damage in a marine environment. Therefore, a comprehensive assessment of marine pollution should ideally include coupled studies linking the levels of pollutants in the seawater with those in the surface sediments, and the seawater and sediment with tissues in various biota. Furthermore, the bio-availability of a heavy metal is critical in the assessment of its damage in the ecosystem. Thus, studies determining the chemical speciation of heavy metals are important.

Conclusions

1. Inorganic geochemical data show that inner and central İzmit Bay surface sediments display high abundances of total organic carbon, S and P, associated with enrichments in Ag, As, Cd, Cr, Co, Cu, Hg, Mo, P, Pb, Sb, Ti, V, and Zn, which are above their pre-industrial background levels. Distribution maps illustrate that heavy metal concentrations are highest in central and inner İzmit Bay, dramatically decreasing near Dil Burnu Entrance.

2. The geo-accumulation indices show that the surface sediments of central and inner İzmit Bay are moderately to very strongly polluted with respect to Ag, Cd, Hg, Mo and Sb, and unpolluted to moderately polluted with respect to As, Co, Cu, Pb, and Zn. Despite total sedimentary concentrations above their pre-industrial background levels, geo-accumulation indices show that the surface sediments in İzmit Bay are unpolluted with respect to Cr, Ti and V.

3. Except for a localized area offshore of Tuzla, outer İzmit Bay is generally unpolluted with respect to heavy metals.

Acknowledgments

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