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The Effect of Marmara (Izmit) Earthquake on the Chemical Oceanography and Mangan Enrichment in the Lower Layer Water of Izmit Bay, Turkey

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1. Introduction

Dissolved oxygen (DO) content of the marine environment is a crucial parameter for life and water quality as well as playing an important role in biogeochemical processes, and respiration of plants and animals, and decomposition of organic matter by bacteria are the primary processes that consume dissolved oxygen content of water and pore-water in sediments. If the oxygen concentration of water falls below about 2 mg/1, living organisms become stressed and the consequent conditions lead to hypoxia. Persistent hypoxia and increased oxygen uptake accompanies release of hydrogen sulfide. Anoxia occurs in estuaries where high loads of organic matter and/or nutrients are supplied, and in semienclosed water bodies where water mixing and tidal exchanges are strongly restricted.

In recent years, aquatic ecosystems have been contaminated by heavy metals; which are of agricultural, industrial, domestic, mining and also natural origins (Ayas and Kolankaya 1996; Han et al., 2002). They are potentially toxic to the aquatic environment; if they exceed natural limits, they will be harmful to the aquatic organisms' environments and human health (Forstner and Witmann, 1981). Organisms need some metals such as Fe, Cu, Zn, Co, Se, Ni and Mn in certain amounts; however, exceeding these amounts may cause toxic effects for these organisms. Some metals such as Hg, Cr, Pb and Cd are toxic to organisms and marine habitat. These metals are dissolved in sea water or suspended in solid materials and absorbed through the gills or skin of marine organisms; they also accumulate in the bodies of organisms through the food chain (Forstner and Witmann, 1981). Mussels, in particular, have been used as biological indicator organisms to monitor marine pollution by toxic heavy metals and potentially toxic chemicals due to their properties of inhabitation (Pempcowiac et al., 1999; Hu 2000).

Izmit Bay (Figure 1) is a semi-enclosed water body and situated in the NE of Marmara Sea. It has been subjected to pollution problems (Orhon et al., 1984; Tuğrul et al., 1989; Morkoç et al., 1996), including eutrophication of the water and inputs of toxic industrial and domestic effluents. Total organic matter load of industrial discharges has been reduced to 80% within the last 10 years, whereas domestic organic loads have been increased in two fold (Morkoç et al., 1996, 2001). The earthquake with a magnitude of 7.4 was occurred at 17th of August 1999, destroying the eastern Marmara Region. The epicenter of the earthquake was found to

be in a small city (Gölcük) located on the southern coast of Izmit Bay. This seismic event caused the destruction of wastewater discharge systems and also dispersal of refined petroleum products onto the sea surface from the subsequent refinery fire. The surface waters of the Bay were partly covered by the thick petroleum layers and partly by a film (Güven et al., 2000, Ünlü et al., 2000). Petroleum layer covering the surface water reduced the transfer of oxygen from air/sea interface and also caused the subsequent death of living organisms. Increasing effluent discharges into the Bay produced an exceptional plankton bloom. Coupling of such factors leading to oxygen deficiency at the sea floor caused the formation of anoxic conditions. Okay et al., (2001) investigated ecological changes in Izmit Bay, however their data is limited with the September 1999.

This paper presents the results of one-year monitoring program performed in Izmit Bay after the Earthquake, with the purposes of describing the abrupt changes in chemical oceanography and understanding the mechanism of H_2S generation in the Bay which has not been occurred before. Furthermore, the factors controlling metal distributions in water column and surface sediments of the Bay were discussed in this study.

1.1 Study area

Izmit Bay is an elongated semi-enclosed water body with a length of 50 km, width varying between 2 to 10 km (Figure 1) and has an area of 310 km^2. The bathymetry of the Bay constitutes three sub-basin separated by shallow sills from each other. The eastern basin is relatively shallow (at about 30 m) whereas the central basin has two small depressions with depths of 160 and 200 m. The western basin deepens in westward from 150 m to 300 m and connects the Bay to the Marmara Sea. Izmit Bay is oceanographically an extension of Marmara Sea, having a permanent two-layered water system. The upper layer is originated from less saline Black Sea waters (18.0-22.0 psu), whereas the lower layer originated from the Mediterranean Sea waters is more saline (37.5-38.5 psu) (Ünlüata et al., 1990). The permanent stratification occurs at about 25 m in the Marmara Sea (Beşiktepe et al., 1994), however it is highly variable in Izmit Bay (Oğuz and Sur, 1986) (Figure 2). The thickness of the upper layer changes seasonally from 9 to 18 m spring and autumn, respectively (Oğuz and Sur, 1986; Algan et al., 1999). The upper layer enters into the Bay in spring and summer, corresponding to the freshwater inflow changes in the Black Sea, while the lower layer flows to the Marmara Sea from the Bay. However, the upper layer flows towards the Marmara Sea in autumn and winter (Oğuz and Sur, 1986). Vertical mixing of the two layers is restricted and occurs at shallow depths. An intermediate layer develops throughout the year in the water column of the Bay with varying thickness (DAMOC, 1971; Baştürk et al., 1985; Tuğrul et al., 1989; Oğuz and Sur, 1986; Altıok et al., 1996). The upper layer of Izmit Bay, in general, is saturated with DO (Tuğrul and Morkoç, 1990). DO concentrations in the lower layer of Izmit Bay has been found to be 2.5-3.0 mgl^{-1} in winter and spring periods and 0.7-1.5 mgl^{-1} in summer, in previous studies (Morkoç, et al., 1996). The minimum DO concentrations have been measured locally in the central basin (0.1-0.2 mgl^{-1}) and in the eastern basin (0.5 mgl^{-1}) during spring-summer period (Tuğrul and Morkoç, 1990). Izmit Bay and its surroundings is one of the most industrialized and populated area of Turkey, receiving more than 300 industrial and domestic effluents (Morkoç et al., 1996). Industrial effluents discharges a total of 163,000 m^3/day wastewater, 24 tons/day BOD and 19,5 tons/day TSS to Izmit Bay (Morkoç et al., 2001). The eastern basin receives the highest inputs compare to other basins of the Bay. Based on the previous studies, no DHS has been measured in Izmit Bay (Morkoç et al., 1988; Tuğrul et al., 1989; Morkoç et al., 1996).

Industrial loads have been reduced by treatment and waste minimization within the last 10 years, but domestic wastes has doubled, due to the increasing population in the Bay. Therefore, the total (domestic + industrial) discharge load into the Bay during the last 10 years has not changed significantly (Morkoç, et al., 2001). The dissolved oxygen content of Izmit Bay decreased dramatically from 1984 to 1999 and reached to a minimum value at 20 m throughout the Bay (Okay et al., 2001). Ergin et al., (1991) suggested that the surface sediments in İzmit Bay are uncontaminated by anthropogenic pollution. However Yaşar et al., (2001) investigated that the heavy metal concentrations are highest in the eastern and central basins. The western basin was also found generally unpolluted with respect to heavy metals by Yaşar et al., 2001.

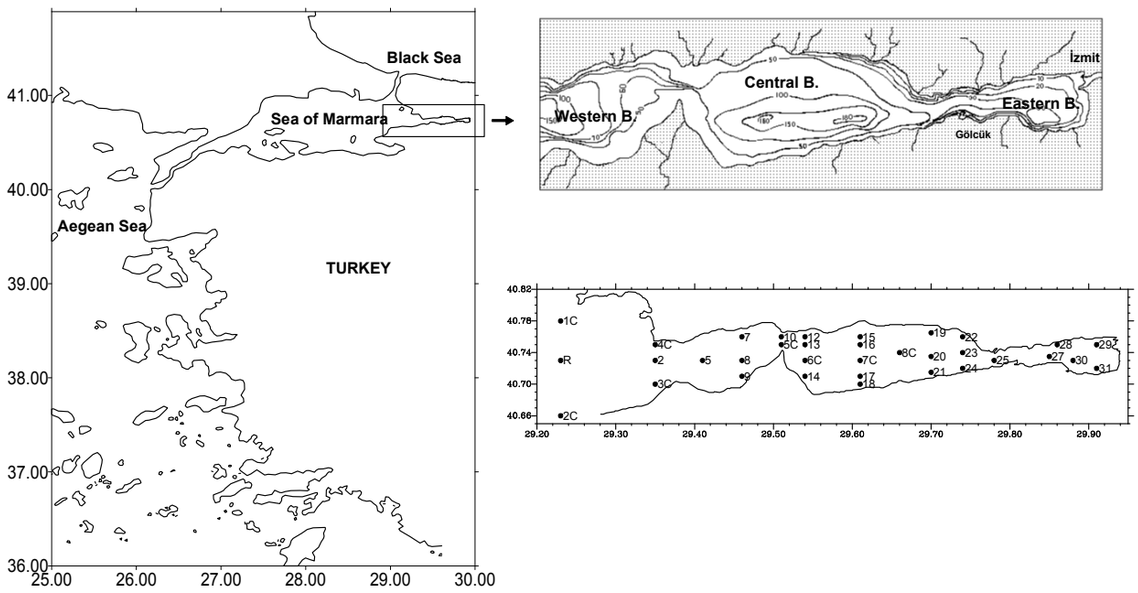

Fig. 1. The location (left) and bathymetry (above) of the study area. The location of sampling station in İzmit Bay (below).

2. Material and methods

2.1 Sampling sites

The water samples were collected from 32 stations in İzmit Bay, including one station located off the western basin (R), on board the R/V Arar (Figure 1). Station (R) represents the characteristics of the Marmara Sea and hence, provides a comparison between the Bay and the Marmara Sea. The sampling stations in İzmit Bay represent the various depths of three basins, with a minimum of 17 m and maximum of 200 m. Sampling was carried out with a Rosette sampler assembled to the Sea Bird CTD System at about 10 m depth intervals through the upper and the lower layers. Sampling period includes August 1999, immediately after the Earthquake and performed monthly in 1999 and in February, May and August during 2000.

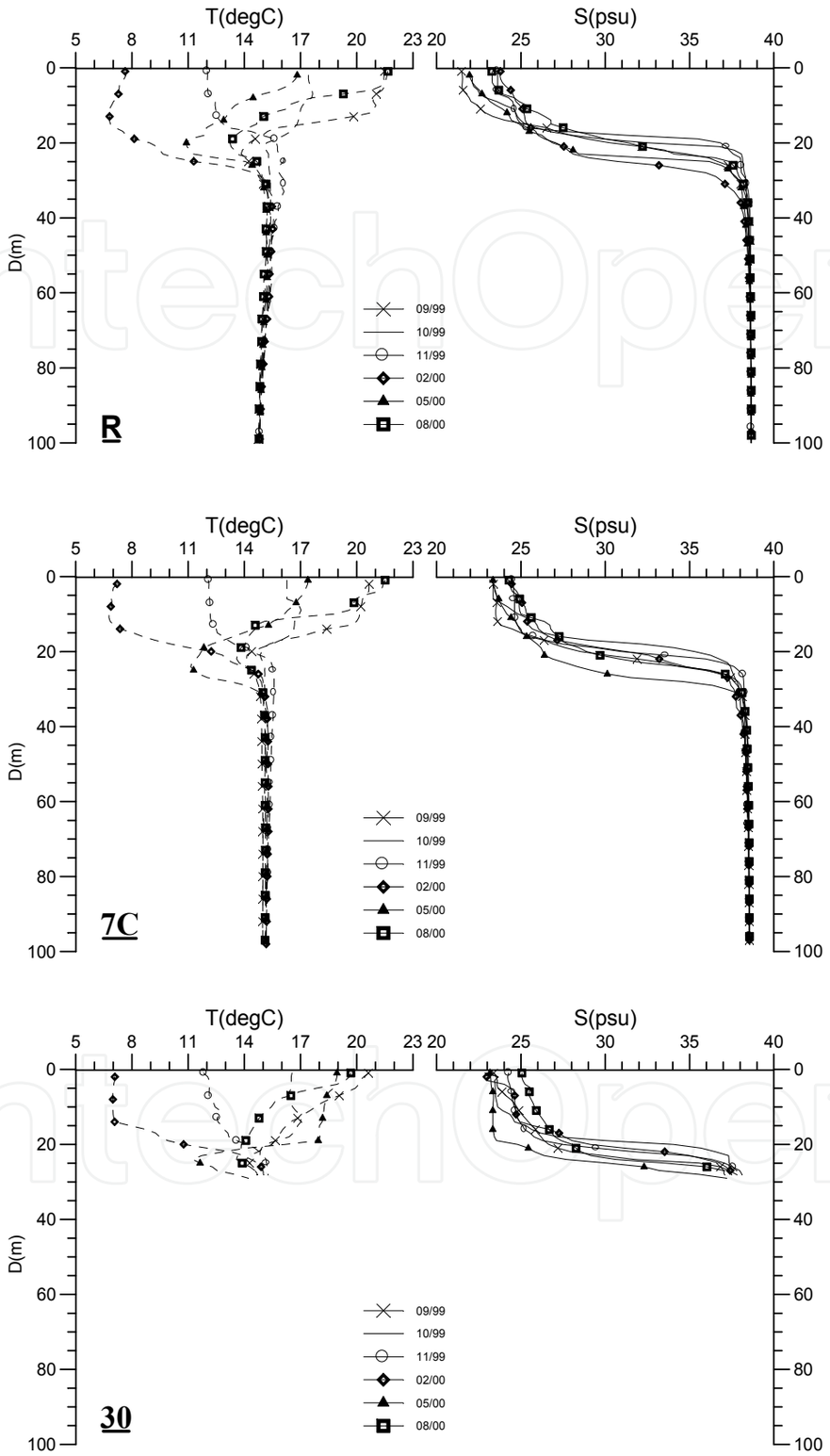

Fig. 2. Depth profile of salinity and temperature distribution along the water column of some selected station from İzmit Bay (from Güven et al., 2000).

2.2 Analytical methods

Samples for DO determinations were drawn first from the Niskin bottles of Rosette to prevent any biological activity and gas exchanges with the atmosphere. DO determination was carried out by Winkler method (Greenberg et al., 1985) on board from all the stations (Figure 1). The precision of method was estimated at ± 1.9 % .

Dissolved hydrogen sulfide (DHS) was measured only at stations where DO concentrations are lower than the detection limit of the method (0.03 mgl^{-1}) (Figure 1), in all the sampling periods, except August and September 1999. DHS contents were measured by an iodometric titration method (Strickland and Parsons, 1972).

pH values measured along the water column at all stations with a WTW 526 pH-meter equipped with a temperature-compensation adjustment on board.

The water samples were filtered through 0.45 μm filters using metal clean tecniques (Bruland et al., 1979). The samples were stored in polyethylene bottles (LDPE) that were acid cleaned using methods described Patterson and Settle (1976). After collection, the samples were acidified to a pH between 1.5 and 2.0 using HNO_3. Dissolved heavy metal concentrations (Fe, Mn, Pb, Cu and Cd) were measured by atomic absorption spectrophotometer (AAS) following preconcentration with ammonium 1-pyrrolidinedithiocarbamate (APDC) in an organic extraction (Bruland et al., 1985). The blanks for the metals analyzed were: Fe, 010 ± 0.05 mg/l; Mn, 0.10 ± 0.02 mg/l; Cu, 0.15 ± 0.08; Cd, 0.05 ± 0.03 mg/l; Pb, 0.20 ± 0.30 mg/l.

The surface sediments total carbonate contents were determined by a gasometric-volumetric method (Loring & Rantala, 1992). Total organic carbon (C_{org}) was analyzed by the Walkey-Blake method, which involves titration after a wet combustion of the sample (Gaudette, 1974; Loring & Rantala, 1992). Al, Fe, Mn, Cu, Zn, Co and Cr contents were determined by atomic absorption spectrophotometer (AAS) after a "total" digestion, involving HNO_3 + $HClO_4$ + HF acid mixture.

The sequential selective extraction analyses were carried out using 1M Na-acetate (pH=5 adjusted by acetic acid) for the dissolution of carbonate phase, 0.04M hydroxylamine hydrochloride (HAHC) in 25% acetic acid for dissolving Fe-Mn-oxyhydroxides, 0.02M nitric acid + 30% hydrogen peroxide (pH=2) for extracting organic matter, and HNO_3 + $HClO_4$ + HF mixture for the total extraction of the residual (lithogenous) fraction (Tessier et al., 1979).

Reference Material	Element	Measured value (this study) ppm	Certified value or range ppm
SL-1	Fe	62	65-7-69.1
IAEA405	Al	63500	72700-83100
SL-1	Cr	98	95-113
SL-7	Mn	634	604-650
CRM-142	Cu	25	27.5
CRM-142	Zn	92	92.4
CRM-142	Co	13	7.9

Table 1. Accuracy of ASS analyses used in this study, as determined by Analysis of AQCS (SL-1 and SL-7), IAEA405 and BCR (CRM 142) reference materials.
SL-1 and SL-7 are lake sediment and CRM 142 is a light sandy soil.

The precision of the "total" metal analyses and the different selective extraction steps is better than 10% and 15%, respectively, at 95% significance level. The accuracy of the analyses were checked by analyzing the AQCS (lake sediment SL-1 and SL-7), IAEA405 and BCR (light sandy soil CRM 142) reference materials (Table 1). The metal values were normalized to eliminate the grain-size effects using metal/Al ratios (e.g., Loring & Rantala, 1992).

3. Results

3.1 Dissolved Oxygen (DO)

The vertical changes of DO in water column are shown by selecting some of the stations from each of the three (western-central-eastern) basins where the variations are significant (Figure 3). In station (R), DO concentrations are between 7.4-10.7 mgl^{-1} for the upper layer, and 1.1-1.5 mgl^{-1} in the lower layer during the sampling period between August 1999 to August 2000 (Figure 3), which are similar to vertical DO concentrations of the Marmara Sea (Ünlüata and Özsoy, 1986; Ünlüata et al., 1990; Doğan et al., 2000). Depth profile of DO concentration in İzmit Bay displays a sharp decrease at about 20 m below the surface in the western and the central basins, following the water stratification during late summer and autumn (Güven et al., 2000) (Figure 3). In February the gradual decline of DO occurs at about 30 m water depth.

DO concentration of the water column in the eastern basin indicates a more gentle profile, probably due to the vertical mixing of the two layers (Oğuz and Sur, 1986; Altıok et al., 1996) in shallow depths. DO concentration of the upper layer in İzmit Bay varies in a range between 4.5 to 12.1 mgl^{-1} during August 1999-2000 (Figure 4a and b). Saturated DO occurs in the upper layer locally at the eastern basin in October 1999 (Figure 4a, 5). The saturation concentration of DO (SDO) values are determined by the solubility oxygen in sea water as a function of the concurrently measured values of temperature and salinity (Figure 2, 5 and 6). The highest DO concentrations were measured in February 2000 (Figure 4b), whereas the lowest DO concentrations were measured in September 1999 after the earthquake. The distribution of DO concentration in the upper layer is almost homogeneous in August and September 1999. From October 1999 to February 2000, DO concentration of the upper layer significantly increases. The increase of DO concentration occurred subsequently following the maximum phytoplankton bloom in October (Güven et al., 2000). DO concentrations range between 7.9-14.5 mgl^{-1} in October 1999, displaying the highest value in the eastern basin (Figure 4a and 5). The distribution of DO concentration in the upper layer becomes almost homogeneous with a range of 9.0-10.4 mgl^{-1} in December 1999 and slightly increases (10.19-12.12 mgl^{-1}) in February 2000. DO concentrations in the upper layer decrease (6.69-10.57 mgl^{-1}) in spring (May-2000, Figure 4b) and are lower in the eastern basin compare to the central and the western basins of İzmit Bay. In August 2000, DO concentrations lie between 5.0 and 9.4 mgl^{-1}, being relatively high in the central basin.

DO content of the lower layer is significantly lower than that of the upper layer, throughout the sampling period (Figure 3). In August 1999, after the earthquake DO concentrations of the lower layer ranges between 0.0-1.46 mgl^{-1}. DO concentration below the detection limits (<0.03 mgl^{-1}) was measured in areas where the water depth is deeper than 100 m and also in the eastern basin (Figure 7a and b). The lowest DO concentration ranges were measured in September 1999. The deficiency of DO is mostly accompanied with the presence of DHS and

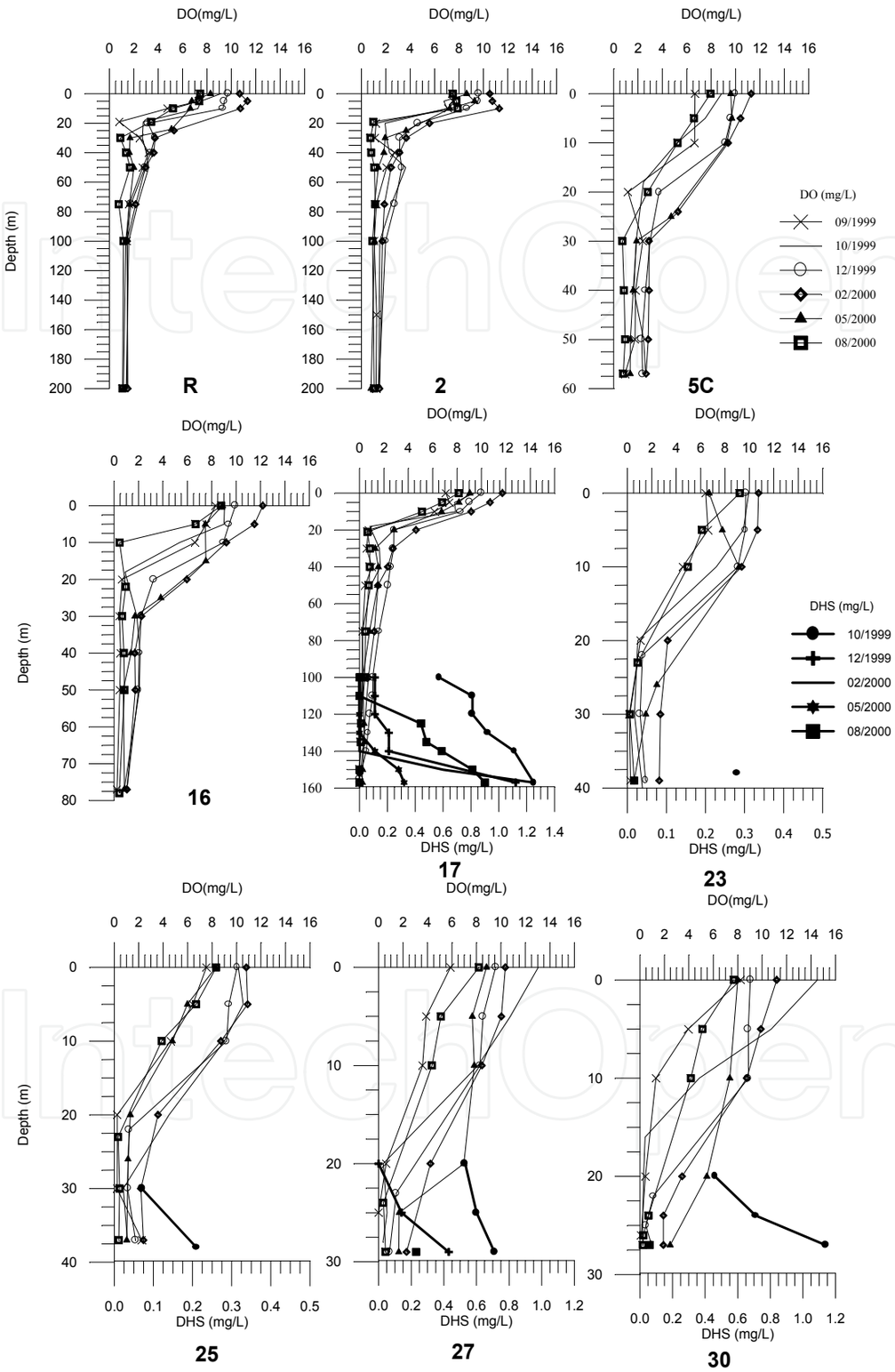

Fig. 3. Vertical distribution of DO and DHS along the water column in various stations of İzmit Bay.

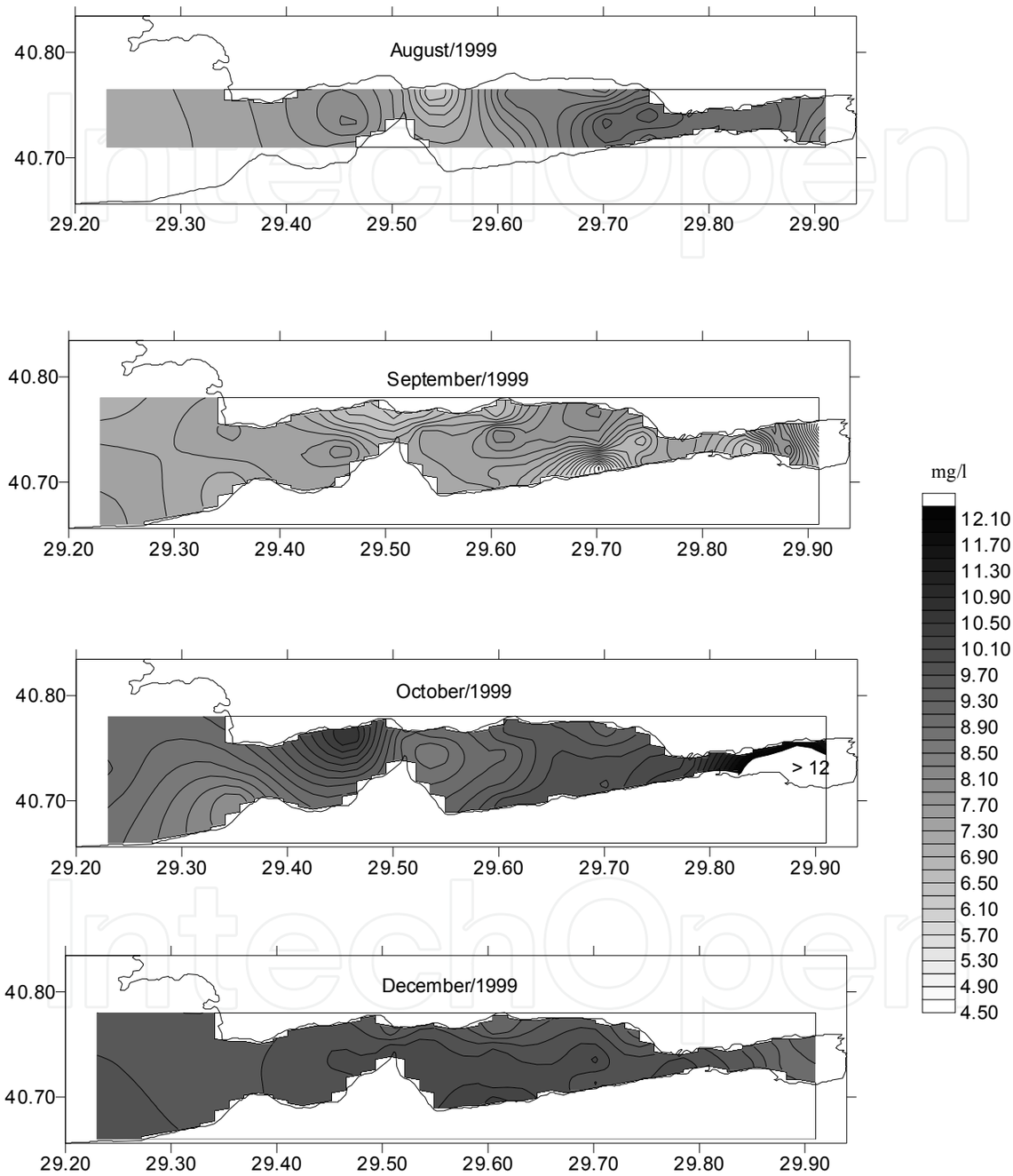

Fig. 4a. Spatial distribution of DO (mgl^{-1}) in the upper layer of İzmit Bay during August to December 1999.

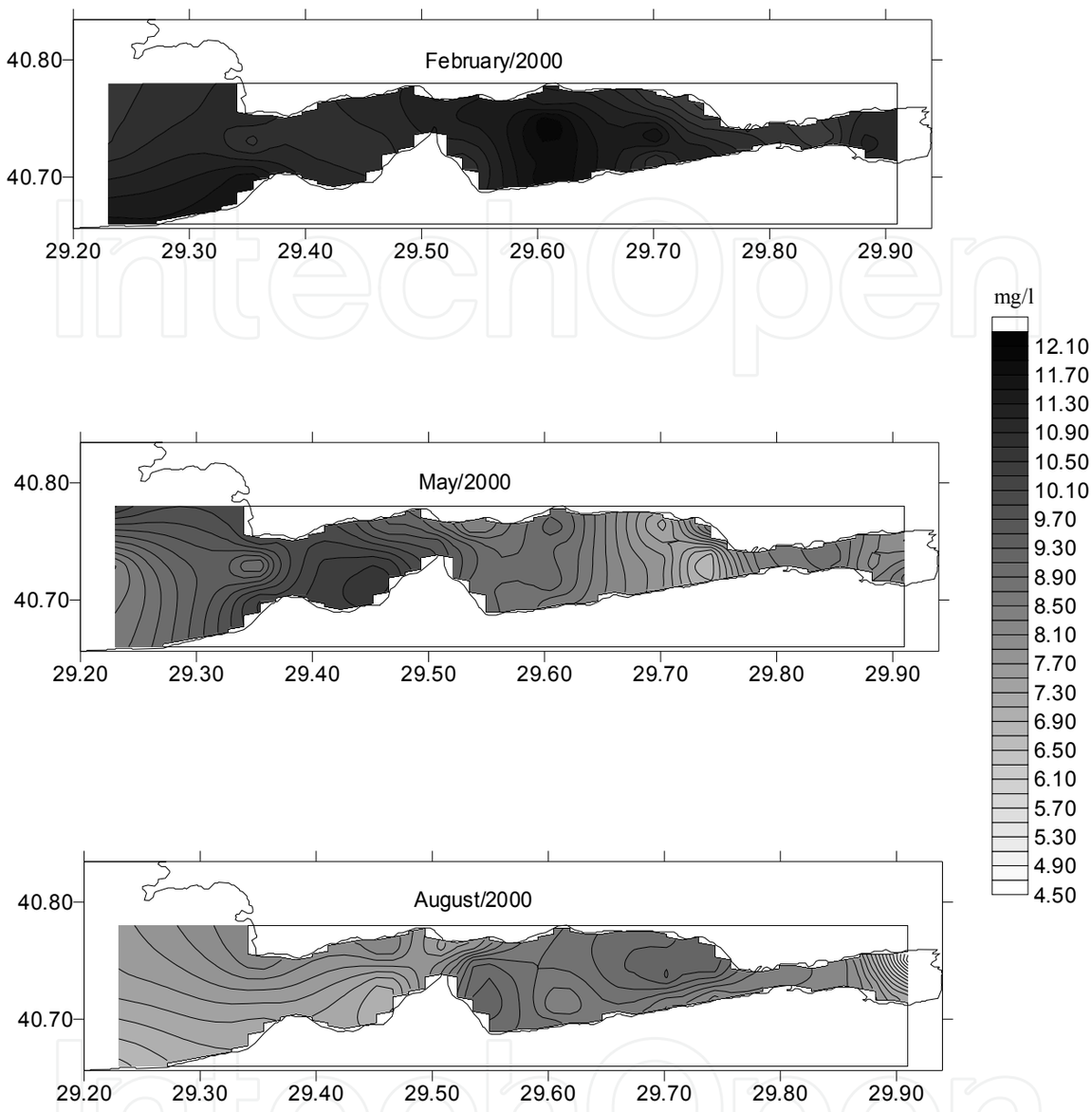

Fig. 4b. Spatial distribution of DO (mgl^{-1}) in the upper layer of İzmit Bay during February to August 2000.

is discussed below. The local anoxic conditions continue in September and October 1999 (Figure 7a), mainly in the central basin with DO concentration range of 0.0-3.4 mgl^{-1} and 0.0-7.9 mgl^{-1}, respectively. In December 1999, DO concentration of the lower layer generally increases (0.0-8.3 mgl^{-1}), but in only one station (17) no DO was lower than the detection limits (Figure 7a). The distribution pattern of DO concentration in the lower layer displays similar behavior in February and May 2000 (Figure 7b) with ranging between 0.0-8.2 mgl^{-1} and 0.0-8.8 mgl^{-1}, respectively. Relatively higher DO concentrations are close to the northern coast of İzmit Bay (Figure 7a and 7b). DO concentration of the lower layer decrease in August 2000, ranging between 0.0-3.6 mgl^{-1}.

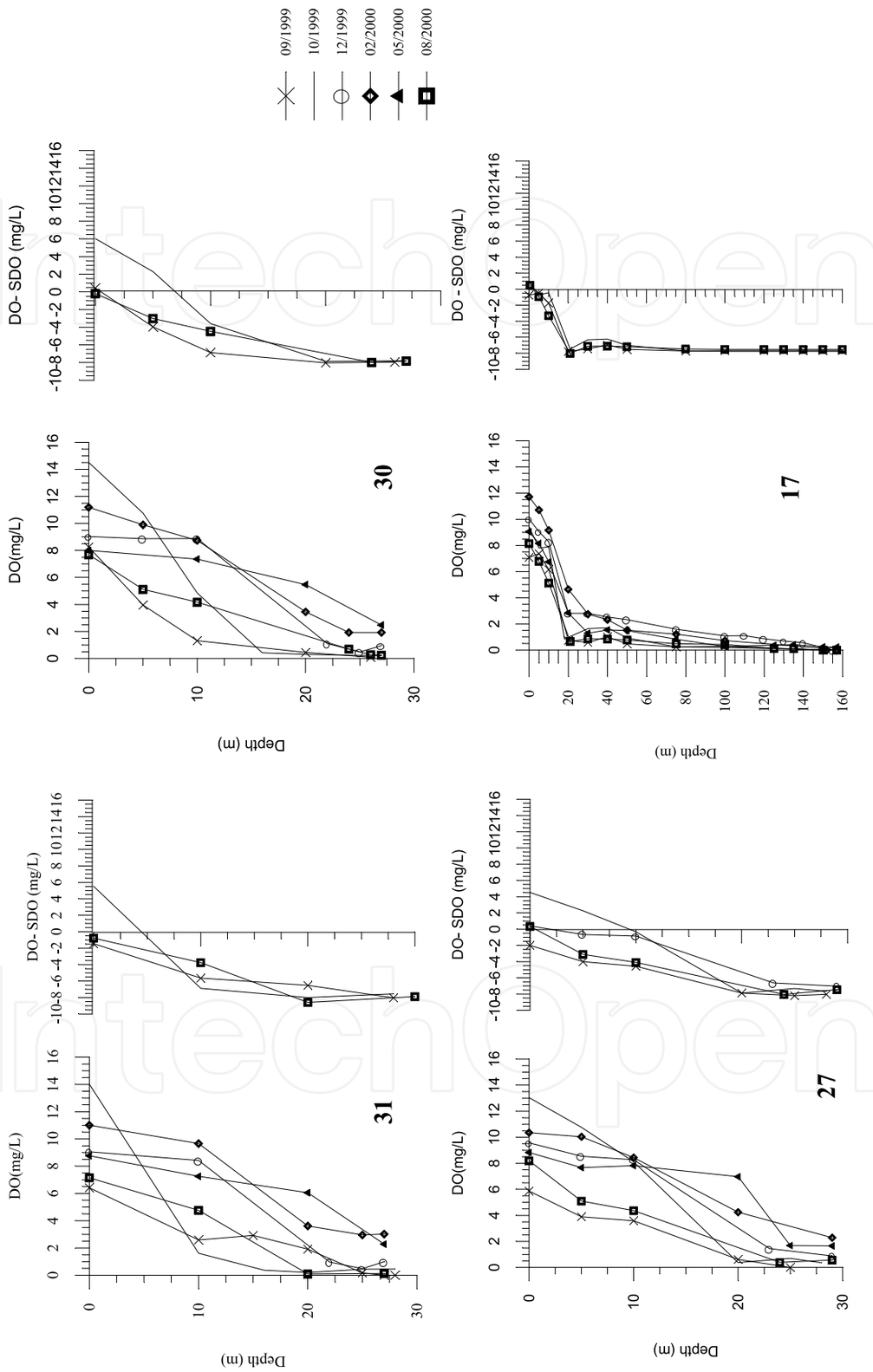

Fig. 5. Oxygen deficiency profiles in some selected stations of İzmit Bay.

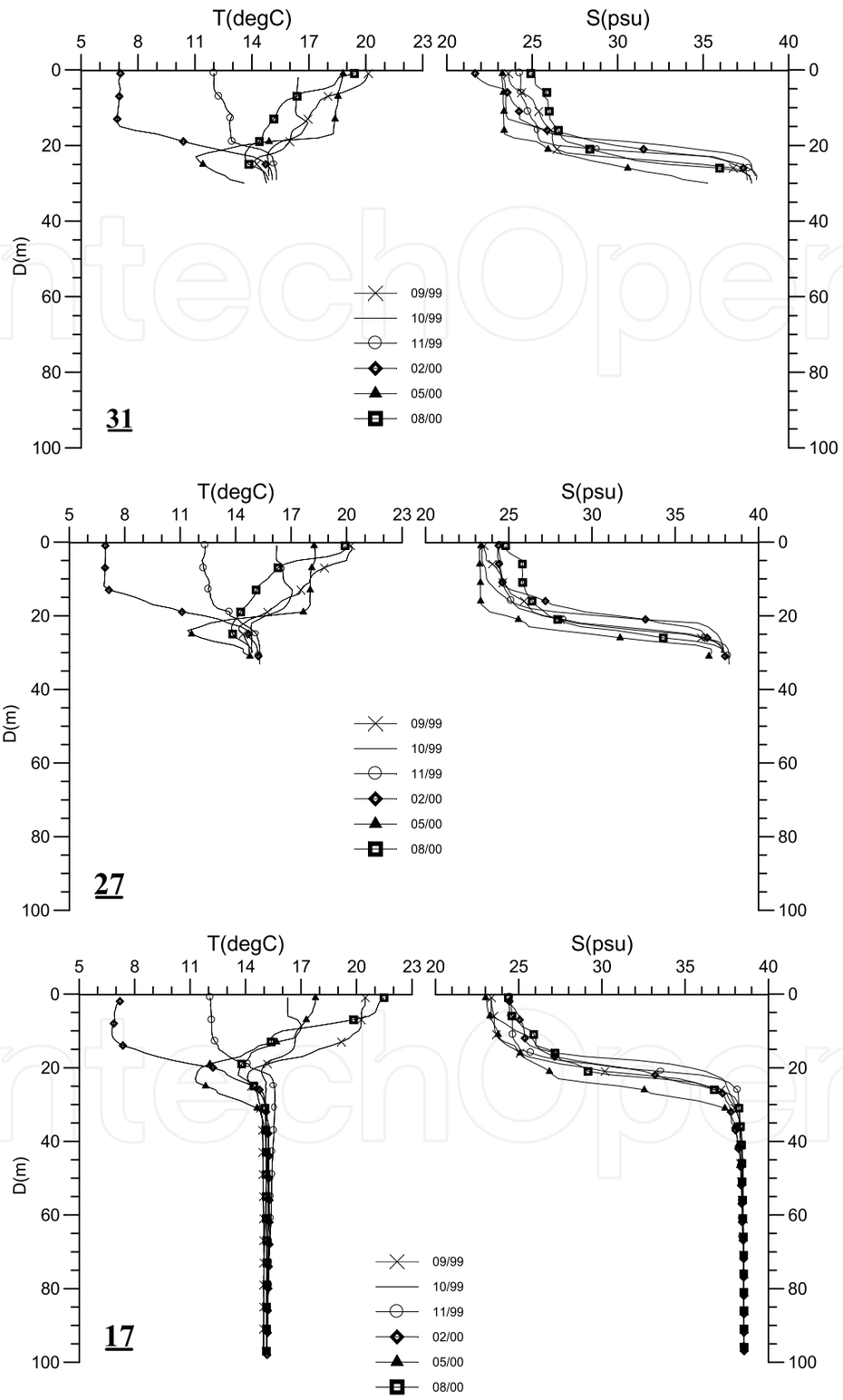

Fig. 6. Depth profile of salinity and temperature distribution along the water column of some selected stations from İzmit Bay (from Güven et al., 2000).

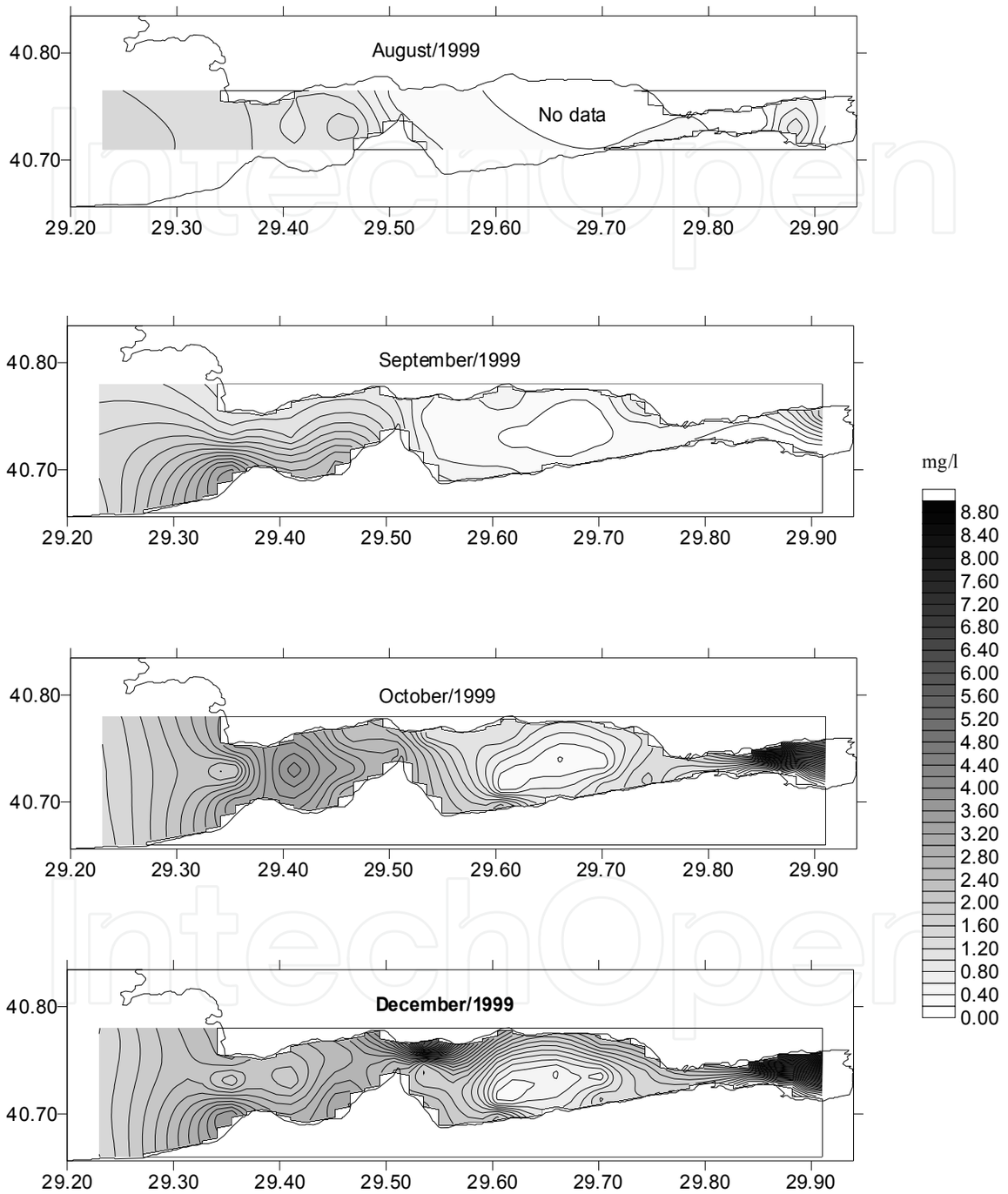

Fig. 7a. Spatial distribution of DO (mgl^{-1}) in the lower layer of İzmit Bay during August to December 1999

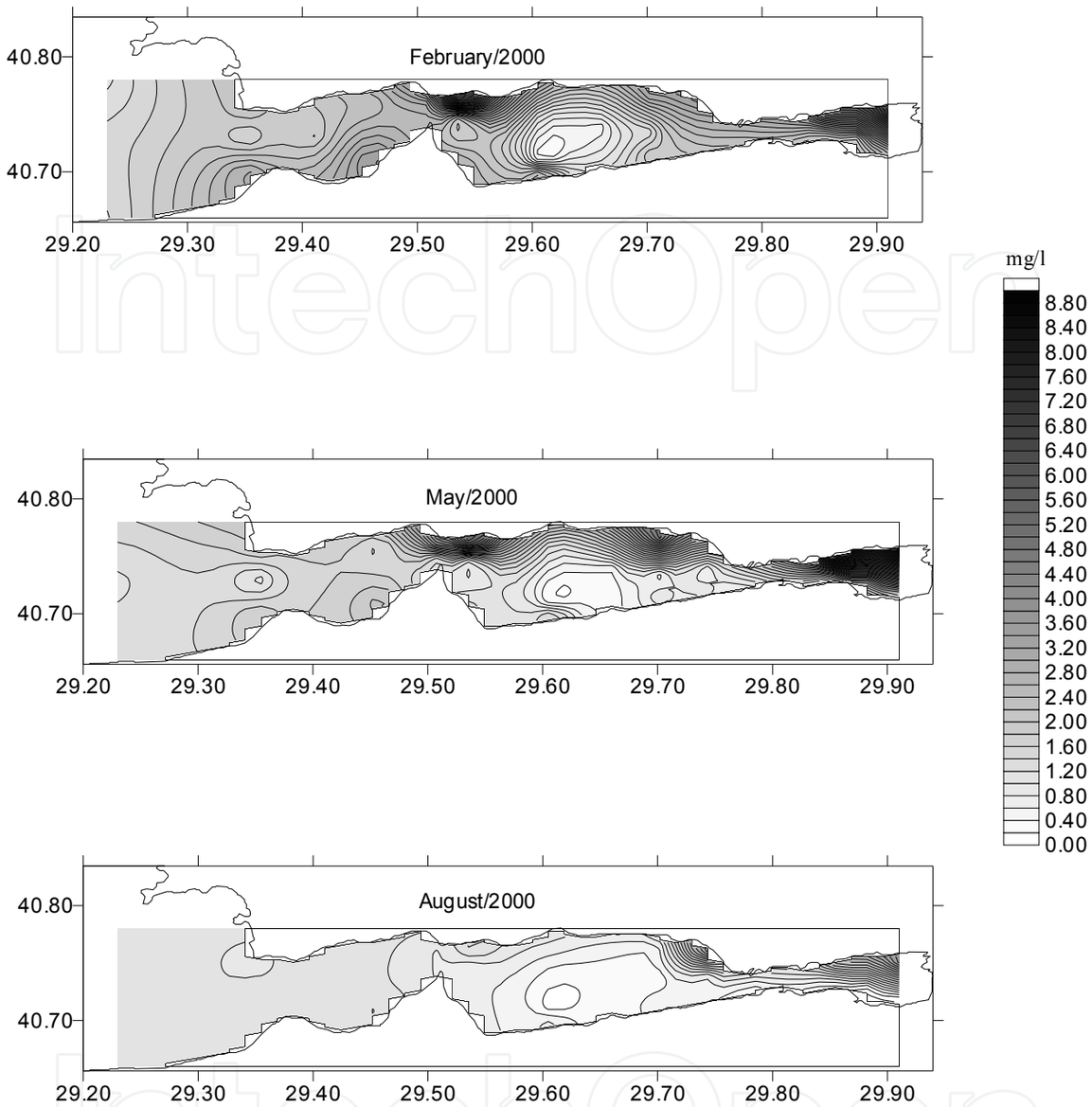

Fig. 7b. Spatial distribution of DO (mgl^{-1}) in the lower layer of İzmit Bay during February to August 2000.

3.2 Dissolved Hydrogen Sulfide (DHS)

The presence of DHS is limited with certain stations and in the lower layer. DHS formation develops both in the shallow area of the eastern basin (maximum 30 m) and relatively deep areas of the central basin. DHS is detected in stations 27, 29, 30 and 31 in the eastern basin, and 8C, 17, 19, 20, 23 and 24 in the central basin (Figure 1, Table 1). In the station 25 situated at the connecting small strait between the eastern and the central basin, measurable DHS exists in the lower layer. DHS concentrations vary in between 0.06-1.25 mgl^{-1}, reaching to their maximum in the lower layer of station 17. No DHS data available for the sampling period of August 1999 after the Earthquake. DHS concentration in October 1999 reaches to 1.14 mgl^{-1} in the eastern basin (station 30) (Figure 3). In general, DHS appears at a water

depth of 20 m in the shallow parts of the eastern basin, with the exception of station 29 where DHS exists up to 10 m to the surface. In December, DHS formation occurs only in stations 27 and 29 and disappears in the other stations. During winter and spring sampling period, no DHS is detected in the eastern basin. Low DHS concentration (0.06 and 0.23 mgl^{-1}) is found in stations 27 and 30 in August 2000.

The central basin							
Station	Water depth (m)	Sampling depth (m)	October 1999	December 1999	February 2000	May 2000	August 2000
25	40	30	0.07	*	*	*	*
		38	0.21	*	*	*	*
27	31	20	0.53	*	*	*	*
		25	0.60	0.14	*	*	*
		29	0.71	0.40	*	*	0.23
29	18	10	0.43	*	*	*	*
		15	0.50	*	*	*	*
		17	0.85	0.24	*	*	*
30	29	20	0.45	*	*	*	*
		24	0.71	*	*	*	*
		27	1.14	*	*	*	0.06
31	30	20	0.28	*	*	*	*
		25	0.28	*	*	*	*
		27	0.36	*	*	*	*
The eastern basin							
17	160	100	0.57	0.11	*	*	*
		110	0.81	0.11	*	*	*
		120	0.81	0.11	*	*	0.43
		130	0.92	0.21	*	*	0.48
		140	1.11	0.21	*	0.11	0.59
		150	-	-	0.60	0.28	0.81
		152	-	-	0.89	-	-
		157	1.25	1.12	1.25	0.32	0.90
8C	116	100	0.64	*	*	*	*
		114	0.93	*	*	*	*
19	29	25	0.40	*	*	*	*
20	106	75	0.28	*	*	*	*
		80	0.40	*	*	*	*
		90	0.43	*	*	*	*
		102	0.71	0.32	*	*	*
23	43	38	0.28	*	*	*	*
24	57	53	0.28	*	*	*	*

(*) No detectable DHS

Table 2. DHS concentrations in the lower layer of the eastern and the central basins of İzmit Bay.

DHS is continuously detected in station 17 from the central basin in all the sampling periods, being highest in October 1999 and lowest in May 2000. The occurrence of DHS corresponds to depth interval of 100-160 m (bottom) during October and December 1999. In February 2000, DHS concentration is limited with the lower 10 m water column, increasing to 1.25 mgl^{-1} at the bottom. The thickness of DHS formation layer slightly increases to 20 m in May 2000, however the concentrations are reduced compare to February 2000 (Figure 3, Table 2). In August 2000, both concentration and thickness of DHS formation of the lower layer in station 17 increase. In spite of continuous presence of DHS in station 17, it occurs solely in October 1999 in the other stations of the central basin, and never reaches to 1 mgl^{-1} (Figure 3, Table 1). DHS is detected mainly at the very close to bottom (2 m above the sea floor) of the lower layer in most of the stations in the central basin, however the lower 25 m and 15 m of the water column in station 20 and 8C, respectively, contain DHS.

3.3 pH

The highest pH values were measured in October 1999 and May 2000 throughout the water column in İzmit Bay, and were particularly high in the eastern basin (Figure 8 and 9). The lowest pH values, on the other hand, correspond to sampling period of August 2000. pH values significantly decrease from 8.5 to 7.1 mainly in the eastern basin and to a lesser degree in the central basin, during the formation of DHS.

3.4 Metals

3.4.1 Water column

Iron concentrations range between <4 mg/l and 21 mg/l along the water column in İzmit Bay (Table 3). The highest values are measured after the Earthquake (October-1999). High dissolved Fe concentrations indicate reduction of Fe-oxides by bacteria during mineralization of organic carbon in the sediment and diffusion into bottom waters (Nealson, 1982; Lovley and Phillips, 1988; Nealson and Myers, 1990). Fe values are decrease in May and August 2000 where Fe limitation is thought to control phytoplankton productivity.

Manganese concentrations vary between <1 and 123 mg/l in water column of the Bay (Table 3). The values increased in lower layer water and near the sediment-water interface in eastern and central basins. This was attributable to the degradation of settling organic carbon (Nealson, 1982; Nealson and Saffarini, 1994; Nealson and Myers, 1990). Manganese oxides were reduced to dissolved Mn^{+2}, which diffused from the sediment into the water column occurring the anoxic conditions. The lowest Mn values are obtained in December 1999 and February 2000. In these periods, oxygen-rich waters of Marmara Sea (Mediterranean originating) flow into the Bay. Thus, Mn-oxides are occurred and flocculated in water column with reoxidation of dissolved Mn in more oxygenated waters.

Lead concentrations range between <0.8 and 1.8 mg/l in the Bay waters (Table 3). The highest values are suggested that atmospheric and anthropogenic inputs.

Copper concentrations vary between <0.4 and 7.4 mg/l along the water column of the Bay (Table 3). The high values shows that Cu was mainly affected by redox reactions involving Mn and Fe in bottom waters of the eastern and central basins. The lowest Cu concentrations are measured in occurring the extreme phytoplankton blooms periods especially in these regions.

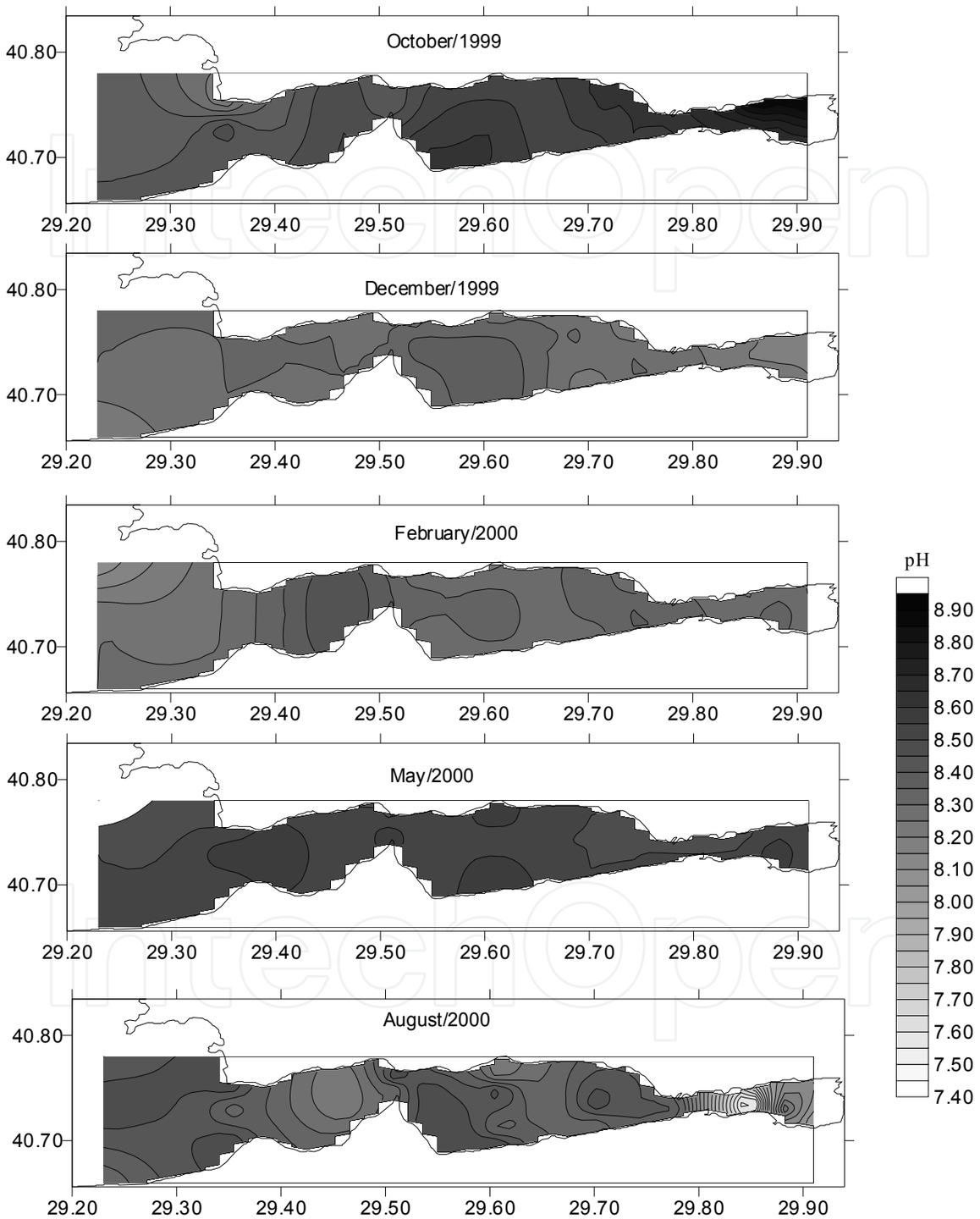

Fig. 8. Spatial distribution of pH values in the upper layer of İzmit Bay.

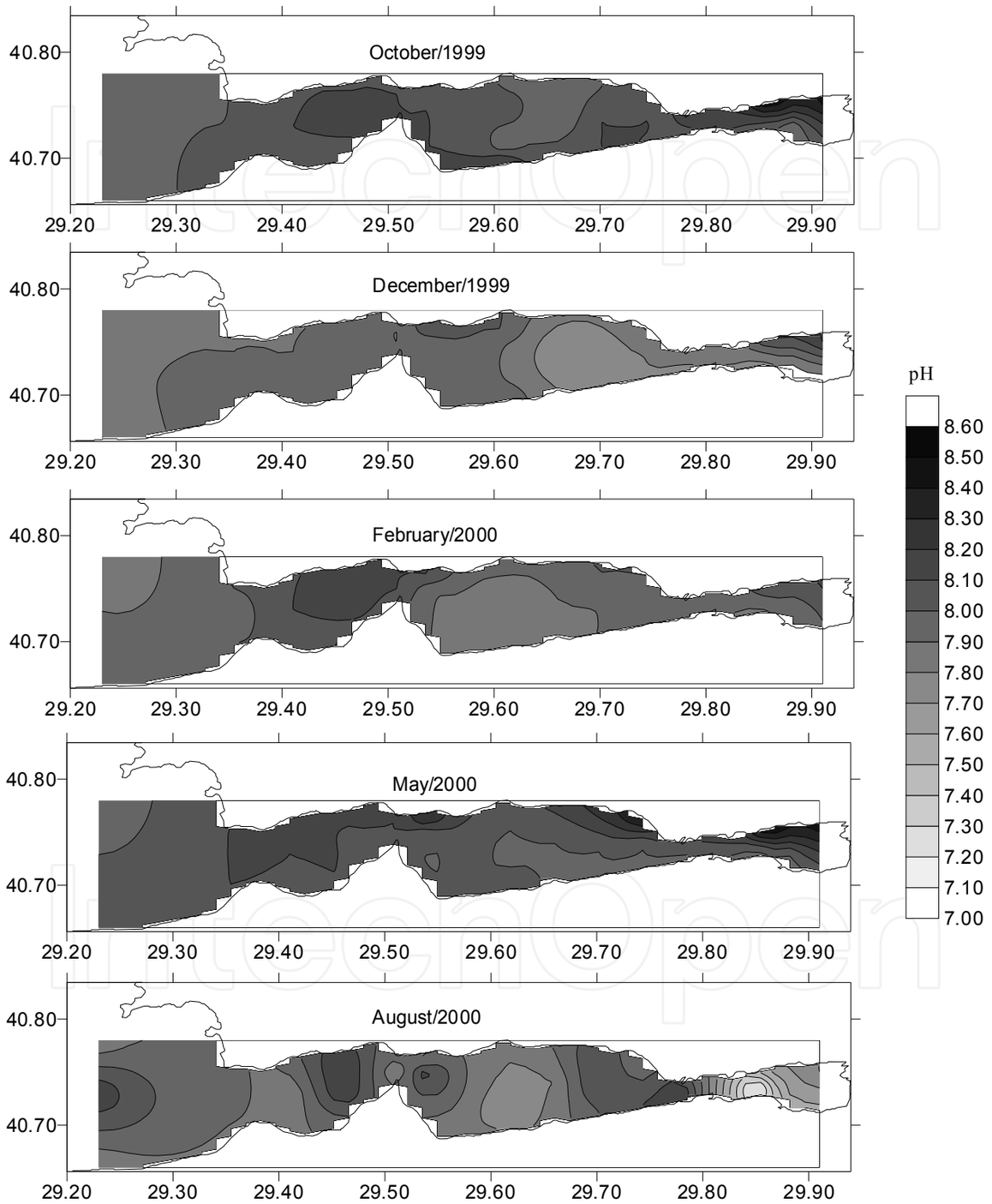

Fig. 9. Spatial distribution of pH values in the lower layer of İzmit Bay.

Element	October 1999	December 1999	February 2000	May 2000	August 2000
Fe	7-15	<4-4	<4-13	<4	<4
Mn	<1-4	1-7	2-4	4-12	<1-13
Pb	<0.8-1	<0.8-0.9	0.9-1	<0.8-2	<0.8-1
Cu	0.5-0.7	0.5-0.9	0.4-0.8	<0.4-0.6	<0.4-0.8
Cd	<0.1	<0.1	<0.1	<0.1	<0.1

Table 3. Metal concentrations along the water column of the Izmit Bay (µg/l).

Cadmium concentrations are lower than the detection limit of the method (<0.01 mg/l) along the water column of the Bay (Table 3). Since the domestic and industrial waste-water system has been damaged by the earthquake, causing the extreme phytoplankton bloom (Okay et al., 2001). This element is incorporated into organic matter by phytoplankton during periods of primary production (Sunda and Huntsman, 1995). Therefore, the relatively low residence time could be the result of biological uptake.

3.4.2 Surface sediments

3.4.2.1''Total'' metal distributions

The Iron concentrations range between 2.4 % and 11.8 % and are generally above the shale average value of 4.7 % (Krauskopf, 1979) (Table 4). The highest values are measured in southern shelf and eastern basin of the İzmit Bay. The Fe distribution in the Bay sediments is controlled mainly by the riverine and anthropogenic inputs on this land-locked system.

Element	Average shale (Krauskopf, 1979)	Gulf of Izmit min - max	Gulf of Izmit mean - SD
Cu (µg/g)	50	11- 42	23 ± 8.87
Zn (µg/g)	90	84 - 306	149 ± 57
Fe (%)	4.7	4.6 - 7.1	6.1 ± 0.6
Mn (µg/g)	850	139 - 494	327 ± 89
Co (µg/g)	20	6 - 20	12 ± 3.93
Cr (µg/g)	100	34 - 77	58 ± 11
Al (%)	9.2	2.3 - 11.4	7.4 ± 2.5
CaCO3	6.0[a]	13 -42	13.4 ± 9.9
Corg (%)	0.8[a]	0.6 - 6.2	3.0 ± 1.6

[a] From Mason and Moore (1982, p.153)

Table 4. Range of metal concentrations of bulk surface sediments from different parts of the Marmara Sea

Manganese concentrations are in general, lower than the average abundance of this element in shale (<850 µg/g). The values increase in western basin of the Bay. Here, Mn^{+2} form of this redox sensitive element derived from the early diagenesis of the sediments, is believed to have been oxidized and flocculated by the oxygen-rich lower layer waters of the Marmara Sea (Mediterranean originating).

The Copper, Cobalt and Chromium concentrations are in general, below the shale average values of 50, 20 and 100 µg/g (Krauskopf, 1979) (Table 3). The highest values in eastern basins surface sediments shows that the anthropogenic inputs from the industrialized regions in here. The Cu values show high correlation with the C_{org} content (r=0.81, Table 4).

Element	Al (%)	Fe (%)	Mn (µg/g)	Cu (µg/g)	Zn (µg/g)	Co (µg/g)	Cr (µg/g)	CaCO3 (%)	Corg (%)
Al (%)	1	+0.22	-0.13	+0.17	+0.17	+0.39	+0.30	-0.57	+0.1
Fe (%)		1	-0.03	+0.37	+0.44	+0.14	+0.54	- 0.32	+0.22
Mn (µg/g)			1	-0.28	-0.32	-0.12	+0.08	+ 0.1	-0.20
Cu (µg/g)				1	+0.89	+0.55	+0.66	- 0.39	+0.81
Zn (µg/g)					1	+030	+0.61	-0.28	+0.78
Co (µg/g)						1	+0.39	-0.56	+0.46
Cr (µg/g)							1	-0.59	+0.55
Corg (%)								1	-0.1
CaCO3 (%)									1

Table 5. Corelation coefficient of matrix geochemical parameters of sediments.

Zinc concentrations range between 84 µg/g and 306 µg/g and are above the shale average value of 4.7 % (Krauskopf, 1979) (Table 4). The high values seem to have been controlled mainly by the anthropogenic inputs from the eastern region similar to the other elements. This element shows a high correlation with the C_{org} and Cu contents (r=0.78, and 0.89 respectively) (Table5).
Al, Fe, Mn, Co and Cr values do not show any significant correlation with the C_{org} content (Table 5).

3.4.2.2 Selective extraction analysis

Sequential exraction analysis were performed to determined the anthropogenic and /or natural inputs on metal distributions in the bay surface sediments. Metal contents of the geochemical phases were given in Table 6.
The highest values of Al, Fe, Zn, Co, and Cr varied between 2.2 % with 10.9 %, 3.8 % with 5.4 %, 18 % with 98 %, 4 % with 9 %, and 12 % with 51 % in the residual phase, respectively. In contrast, the highest values of Cu and Mn ranged from 6 % to 26 % in organic phase and from 32 % to 276 % in the Fe-Mn oxyhydroxide phase, respectively. While Fe and Cr values were generally lower than the detection limit of the methods (<0.05 and 0.08 µgL-1) in the exchangeable and carbonate phases, Al contents were also detected in the organic and residual (lithogenous) phases. Zn and Mn showed the highest values in Fe-Mn-oxyhydroxide phase, but Cu those in the organic phase along the bay. In addition, Cu, Zn, Mn and Co levels were relatively high in all geochemical phases.

Element	Exchangable phase	Carbonate phase	Fe-Mn-oxyhydroxide phase	Organic phase	Residual phase
Cu (ppm)	0.3-1.1	0.3-1	1.3-4.5	6-26	4-14
Zn (ppm)	0.1-2.3	0.8-37	15-121	14-46	18-98
Fe (%)	<0.05	<0.05	0.1-0.6	0.5-1.1	3.8-5.4
Mn (ppm)	1-13	6-51	32-276	32-241	32-176
Co (ppm)	0.1-1.3	0.1-2.2	0.3-3.7	0.2-9	4-9
Cr (ppm)	<0.08-4.5	<0.08	1.4-24	2-23	12-51
Al (%)	<0.03	<0.03	<0.03	0.1-0.4	2.2-10.9

Table 6. Metal distributions in different geochemical phases (%).

4. Discussion

DO concentrations of the water column were low in August 1999, after the earthquake, compare to that of other sampling periods. The low DO content was determined in all the stations of İzmit Bay, and particularly in the lower layer waters of the eastern and the central basins, being lower than the detection limit of the method (0.03 mgl^{-1}) (Figure 7b). The negative DO–SDO value along the water column suggested that the oxygen utilization was resulted from the decomposition of organic matter (Figure 5). The limited air-water exchange of free oxygen caused by the spreading petroleum from the refinery fire to the sea surface might be one of the main reason for lowering of DO content in water column. The highest oil concentration was determined in surface water of south of the central basin as 179.2 mgl^{-1} in August 1999 (Güven et al., 2000, Ünlü et al., 2000). The oil concentrations of the surface water are more than 500 μgl^{-1} in almost half of the western and central basins after the earthquake. In spite of high oil pollution levels of the surface water, the oil concentrations in the lower layer are between 13-55 μgl^{-1}in the Bay exception of north of the central basin in August 1999. This oil pollution level decreased to 10.5 mgl^{-1} in September 1999 and 3.3 mgl^{-1} in October 1999. The upper layer flows westward to Marmara Sea, while the lower layer flows into the Bay transporting oxygenated Mediterranean originated Marmara Sea waters in September and October 1999 (Güven et al., 2000). This current system provided the removal of the petroleum layer at the sea surface from İzmit Bay to the Marmara Sea and consequently DO concentrations increased in the water column accompanied by phytoplankton bloom (Figure 4a). Phytoplankton bloom was intense in the eastern basin (2,553,000 cell/l, Güven et al., 2000) and possibly the reason for the saturated DO content in this part of the Bay (Figure 5). Since the domestic and industrial wastewater system has been damaged by the earthquake, the nutrient input into the Bay increased, causing the extreme phytoplankton bloom (Okay et al., 2001). In spite of high DO concentrations of the upper layer, DHS is found in the lower layer of the eastern and the central basins (Figure 3). This striking condition clearly indicates the excess organic load that rapidly depositing at the bottom of

the Bay. Although no DHS data is available for the previous sampling period (August and September 1999), the establishment of this anoxic condition at the bottom might have started to develop earlier than October 1999. Earlier studies related to the ocenographic features of the Bay have never determined anoxic conditions in the water column (Morkoç, et al., 1988; Tuğrul et al., 1989; Morkoç et al., 1996).

The Marmara Sea water flows as the upper layer into the Bay in December 1999 and the current system is towards the interior of the Bay, whereas the lower layer flows out of the Bay (Güven et al., 2000). The available DHS formation in the eastern and the central basins is reduced or completely disappears in this month by the outflow of the lower layer (Table 2). This current system becomes reversed in February 2000, entering the lower layer and out-flowing the upper layer. The significant increase of DO concentrations of the upper layer in February 2000 might possibly indicate the replenishment of water column in İzmit Bay with oxygenated waters. This is in agreement with the vertical and spatial distribution of DO concentrations in February (Figures 3 and 4b). The thickness of the upper layer increases to 25-30 m suggesting the entrance of waters into the Bay. DO content of the both the upper and the lower layer slightly decreases in May 2000, together with increasing alkalinity (Figures 4b, 7b, 8 and 9). The reducing DO content in this month might be related with the water influx enriched with nutrients into İzmit Bay from the Black Sea (via the Marmara Sea) that receives increasing amount of freshwater inflow during spring (Oğuz and Sur, 1986; Tuğrul and Polat, 1995). In August 2000, DO concentration of the water column is significantly reduced (Figures 4 and 6), suggesting the enhanced consumption of DO by decomposition of high organic materials that possibly from the subsequent death of blooming phytoplanktons. In the eastern basin, the lowest pH is found in this month, supporting the increasing decomposition processes and the formation of DHS (Figure 9).

The formation of DHS leading to anoxia at the lower layer of İzmit Bay occurs in the eastern basin where the depths are shallower than 30 m and also locally in the deep site of the central basin where circulation is restricted (Table 2). After the Earthquake, in the central and the eastern basins, the formation of DHS is resulted from the spreading petroleum from the refinery fire to the surface waters and accumulation of high amounts of organic load from the damaged wastewater systems, and resuspension of bottom sediments releasing the DHS in the anoxic part of the sediment column. This is in agreement with the low DO concentrations of the water column in İzmit Bay during August and September 1999 (Figures 4a, 7a). The removal of anoxia at the bottom of the eastern and the central basins occurred in December 1999 by the replacing of water layers with the oxygenated Marmara Sea waters. DHS exists in the lower layer consistently throughout the sampling period in station 17 (Table 2), however its thickness varies. The reduced bottom current velocities (Algan et al., 1999) and topographic restriction of this small depression might be the reasons for the presence of DHS, by preventing the circulation.

In August 2000, DHS forms again in the eastern basin in low concentrations (Table 2). This re-occurrence of DHS is related with the extreme phytoplankton bloom. A high amount of organic matter produced from their death consumes oxygen for decomposition in the sediment. High decomposition rates might have led the depletion of DO in the overlying water column and consequent formation of DHS. The seasonal circulation pattern and timing of blooms in İzmit Bay were not different than the present as indicated by the

previous studies (Oğuz and Sur, 1986; Tuğrul et al., 1989; Morkoç et al., 1996). DO content has never been fallen below 0.5 mgl^{-1}, and no DHS has been detected in İzmit Bay. Therefore, the re-occurrence of DHS a year after the Earthquake might indicate that İzmit Bay has not been completely return to its regular chemical oceanography. This may be explained by the fact that the amount of organic and possible inorganic wastes into İzmit Bay must have been considerably high and/or must have continued to discharge after the Earthquake. Increasing nutrients, phytoplankton blooms, rapid sedimentation of death organisms and decomposition processes constituted a successive cycle in İzmit Bay and intensified by the Earthquake at 17th August 1999. However, decomposition processes within this cycle might not be completed within a year.

The highest pH values found (8.9) at the upper layer compare to other months in the eastern basin confirms the increasing biological activity in October 1999 (Figure 8). During the respiration of phytoplanktons, dissolved CO_2 content of water column increases and consequently CO_3^{-2} and HCO_3^- anions increase. Increasing carbonate causes enhancement of alkalinity. The pH values become 7.9 at the lower layer (Figure 9) where the anoxic conditions are developed (Figure 3) and indicate the decomposition of organic matter.

Total metal contents in the İzmit Bay sediments increase towards to eastern basin. The eastern basin receives the highest inputs compare to other basins of the Bay (Morkoç et al., 2001). Ergin et al., (1991) suggested that the surface sediments in İzmit Bay are uncontaminated by anthropogenic pollution. However Yaşar et al., (2001) investigated that the heavy metal concentrations are highest in the eastern and central basins. The western basin was found generally unpolluted with respect to heavy metals in this study, also.

Selective extraction studies indicate that the metals are mainly found in the lithogenous, Fe-Mn-oxvhydroxide and organic fractions (Table 6). The results show that the main source of high metal concentrations in the İzmit Bay sediments is of anthropogenic origin. The highest metal values in these fractions are found in eastern basin sediments similar to total metal distributions.

5. Conclusions

Izmit Bay have been polluted by increasing industrial activities and domestic discharges since early 1980. However this abrupt event caused short-time drastic changes in the water column. Earthquake at 17 August 1999 initiated a fast variation in the chemical oceanography of polluted Izmit Bay. This variation includes the consumption of DO and formation of DHS in the lower layer. The refinery fire and damaged municipal waste effluents caused the reduction of DO in water column by preventing the oxygen transfer from air/ water contact and increasing organic wastes, respectively, and as a result DHS was formed. The increasing wastewater into the Bay stimulated the phytoplankton blooms that causes locally saturated DO concentrations in the eastern basin, however anoxic conditions were prevailing in the lower layer during autumn 1999. The changing circulation pattern during winter provided replenishment of the water column in Izmit Bay and removal of DHS. However, DHS formation established again in August 2000.

The distribution of total metals (Fe, Pb, Cu, Zn, Co, Cr and Cd) in both the water-column and surface sediments showed the influences of terrestrial anthropogenic inputs in the bay. The Mn enrichment in the lower-layer water of the central and eastern basins

originated from the occurring anoxic conditions after the Marmara (Izmit) earthquake. Selective extraction studies indicated that the metals were mainly found in the lithogenous, Fe-Mn-oxvhydroxide and organic fractions. The results underlined that the main source of high metal levels in Izmit Bay sediments is of anthropogenic origin. These conclusions reached by the selective extraction studies were supported by the "total" metal distributions along the bay.

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7. References

Algan, O., Altıok, H.. and Yüce, H., 1999. Seasonal Variation of Suspended Particulate Matter in Two-layered İzmit Bay, Turkey. Estuarine, Coastal and Shelf Science 49, 235-250.

Altıok, H., Legovich, T. and Kurter, A., 1996. A case study of circulation and mixing processes in two-layered water system: İzmit Bay. Eight International Biennial Conference on Physics of Estuaries and Coastal Seas, Extended Abstracts, 8-12 September 1996, Netherlands Centre for Coastal Research, pp. 92-96.

Ayas, Z., & Kolankaya, D., 1996. Accumulation of some heavy metals in various environments and organisims at Göksu Delta, Türkiye, 1991-1993. Bulletin of Environmental Contamination and Toxicology, 56, 65-72.

Baştürk, Ö., Tuğrul, S., Sunay, M., Balkaş, T., Morkoç, E., Okay, O.S. and Bozyap, A., 1985. Determination of oceanographic characteristics and assimilation capacity of İzmit Bay. NATO TU-WATERS Project, Technical Report. Kocaeli, Turkey. TÜBİTAK-MRC Publication.

Beşiktepe, Ş.T., Sur, H.İ., Özsoy, E., Latif, M.A., Oğuz, T. and Ünlüata, Ü., 1994. The circulation and hydrography of the Marmara Sea. Progress in Oceanography 34: 285-334.

Bruland, K. W., Franks, R. P., Knauer, G.A., Martin, J. H., 1979. Sampling and analytical methods for the determination of copper, cadmium, zinc and nickel at the nanogram per liter level in seawater. *Anal. Chim. Acta* 105, 233-245.

Bruland, K. W., Coale, K. H., Mart, L., 1985. Analysis of seawater for dissolved cadmium, copper and lead: an inter comparison of voltametric and atomic adsorption methods. *Mar. Chem.* 17, 285-300.

DAMOC, 1971. Master plan and feasibility report for water supply and sewerage for Istanbul region. Prepared by the DAMOC Consortium for WHO, Los Angles, CA, Vol. III, Part II and III.

Doğan, E., Sur, H.İ., Güven, K. C., Polat, Ç., Kıratlı, N., Yüksek, A., Uysal, A., Algan, O., Balkıs, N., Ünlü, S., Altıok, H., Gazioğlu, C., Taş, S., Aslan, A., Yılmaz, N. and Cebeci, M., 2000. Su Kalitesi İzleme Çalışması. Technical Report. İSKİ. Deniz Bilimleri ve İşletmeciliği Enstitüsü, Istanbul Üniversitesi. (in Turkish).

Ergin, M., Saysam, C., Baştürk, Ö., Erdem, E. and Yörük, R., 1991. Heavy metal concentrations in surface sediments from the two coastal inlets (Golden Horn Estuary and İzmit Bay) of the northeastern Sea of Marmara. Chemical Geology, 91: 269-285.

Förstner, U. & Witmann, G.T.W., 1981. Metal pollution in the environment (p. 486). Berlin Heidelberg New York: Springer.

Greenberg, A.G., Trussel R.R., Clesceri, L.S., Franson, M.A.H., editors. Standard methods for the examination of water and wastewater, American Water Work Association (APHA, AWWA and WPCF). 16 th ed. Washington, 1985.

Güven, K.C., Sur, H.İ., Okuş, E., Yüksek, A., Uysal, A., Balkıs, N., Kıratlı, N., Ünlü, S., Altıok, H., Taş, S., Aslan, A., Yılmaz, N., Müftüoğlu, A. E., Gazioğlu, C., and Cebeci, M. 2000. İzmit Körfezi'nin Oşinografisi. 17 Ağustos 1999 Depremi sonrası İzmit Körfezi'nde Ölçme ve İzleme Programı. Technical Report. T. C. Çevre Bakanlığı. Deniz Bilimleri ve İşletmeciliği Enstitüsü, Istanbul Üniversitesi. (in Turkish).

Han, X.F., Banin, A., Su, Y., Monts, L.D., Plodinec, J.M. & Kingery, L. W., 2002. Industrial age anthropogenic inputs of heavy metals into the pedosphere. Naturwissen-schaften, 89, 497-504.

Hu, H., 2000. Exposure to metals. Prim. Care, 27: 983-996.

Krauskopf, K. B., 1979. *Intoduction to Geochemistry*, (617 pp). Tokyo: McGraw-Hill Kogakusha.

Loring, D.H., & Rantala, R.T.T., 1992. Manuel for the geochemical analyses of marine sediments and suspended particulate matter. *Earth-Science Reviews,* 32, 235-283.

Lovley, D.R., Pihillips, E.J.P., 1988. Novel mode of microbial energy metabolism: organic carbon oxidation coupled to dissimilatory reduction of iron and manganese. Applied "Environmental Microbiology 54, 1472-1480.

Morkoç, E., Tuğrul, S. and Okay, S.O., 1988. Determination of Limiting Nutrients by Using Algal Bioassay Technique. Wastewater treatment and disposal studies. NATO-TU-WATERS, First Annual Report. TÜBİTAK-MRC Publications, Kocaeli, Turkey.

Morkoç, E., Okay, S.O. and Geveci, A.1996. Towards a Clean İzmit Bay. Technical Report. TÜBİTAK-MRC Publications, Kocaeli, Turkey.

Morkoç, E., Okay, S.O., Tolun, L., Tüfekçi, V., Tüfekçi, H., and Legoviç, T., 2001. Towarsd a clean İzmit Bay. Environmental International 26: 157-161.

Nealson, K.H., 1982. Microbiological oxidation and reduction of Iron: Holland, H.D., Schidlowski, M. (Eds.), Mineral Deposits and Evolution of the Biosphere. Dahlem Konferenzen, Springer, Berlin, pp. 51-56.

Nealson, K.H., Myers, C.R., 1990. Iron reduction by bacteria: potential role in the genesis of banded iron formation. American Journal of Science 290A, 34-45.

Nealson, K.H., Myers, Saffarani, D., 1994. Iron and manganese in anaerobic respiration: environmental significance, physiology and regulation. Annual Review in Microbiology 48, 31-343.

Oğuz, T. and Sur, H.İ., 1986. A numerical modelling study of circulation in the Bay of İzmit: Final Report. TÜBİTAK-MRC, Chemistry Department Publication, Kocaeli, Turkey, No. 187. 97 pp.

Okay, S.O., Legoviç, T., Tüfekçi, V., Egesel, L. and Morkoç, E., 1996. Environmental impact of land-based pollutants on İzmit Bay (Turkey): short-term algal bioassays and simulation of toxicity distribution in the marine environment. Archives of Environmental Contamination and Toxicology 31, 459-465.

Okay, S.O., Tolun, L., Telli-Karakoç, F., Tüfekçi, V., Tüfekçi, H.. and Morkoç, E., 2001. İzmit Bay (Turkey) Ecosystem after Marmara Earthquake and Subsequent Refinery Fire: the Long-term Data. Marine Pollution Bulletin, 42, 361-369.

Orhon, D., Gönenç, E., Tünay, O. and Akkaya, M., 1984. The prevention and removal of water pollution in the İzmit Bay : determination of technological aspects. Technical Report. İstanbul, Turkey: İTU-Civil Eng. Publ., 1984.

Sunda, W.G., Huntsman, S.A., 1995. Cobalt and zinc interreplacement in marine phytoplankton: biological and geochemical implications. Limnol. Oceanogr. 40, 1404-1417.

Strickland, J.D.H. and Parsons, T.R., 1972. A Practical handbook of seawater analysis 2nd. Ed., Oxford press, Ottawa, Bull. Fish. Bd. Can.

Pempcowiac, J., Sikora, A., Biernacka, E., 1999. Specification of heavy metals in marine sediments, their bioaccumulation by musssels. Chemosphere, 39: 313-321.

Tessier, A., Campbell, P. G. C., & Bisson, M., 1979. Sequental extraction procedure for the speciation of particulate trace metals. *Analyt. Chem.,* 51, 844-850.

Tuğrul, S., Sunay, M., Baştürk, Ö. and Balkaş, T.I., 1986. The İzmit Bay case study. In: G. Kullenberg (Ed.), The Role of Oceans as a Waste Disposal Option., pp. 243-275. Reidel, Dordrecht.

Tuğrul,S., Morkoç, E. and Okay, S.O., 1989. The Determination of Oceanographic Characteristics and Assimilation Capacity of the İzmit Bay. Wastewater treatment and disposal studies. NATO TU-WATERS, Technical Report. TÜBİTAK- MRC, Kocaeli-Turkey.

Tuğrul, S. and Morkoç, E., 1990. Transport and water quality modeling in the Bay of İzmit. NATO TU-WATERS Project, Technical Report. TÜBİTAK-MRC Publ. Kocaeli, Turkey.

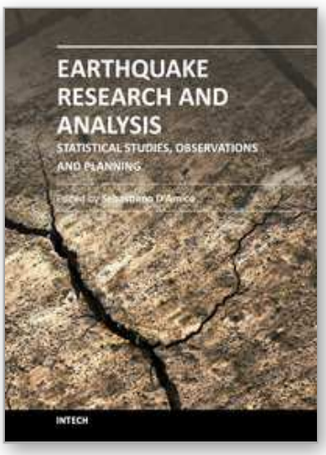
Tuğrul, S. and Polat, Ç., 1995. Quantitative comparison of the influxes of the nutrients and organic carbon into the Sea of Marmara both from anthropogenic sources and from the Black Sea. Water Science and Technology, 32: 115-121 pp.

Ünlüata, Ü., and Özsoy, E., 1986. Oceanography of the Turkish Straits-First Annual Report, Volume II, Health of the Turkish Straits, I. Oxygen Deficiency of the Sea of Marmara, Institute of Marine Sciences, METU, Erdemli, İçel, Turkey, 81 pp.

Ünlüata, Ü., Oğuz, T., Latif, M.A. and Özsoy, E., 1990. On the Physical Ocenography of the Turkish Straits. In: Pratt, L. J., (Ed.), The Physical Oceanography of Sea Straits. Kluwer Academic Publishers, Netherland, pp. 25-60.

Ünlü, S., Güven, K. C., Okuş, E., Doğan, E. and Gezgin, T. (2000). Oil Spill Tüpraş Refinery Following Earthquake occured in 17 Aug 1999. Second International Conference, Oil Spills in the Mediterranean and Black Sea Regions, pp. 1-11, Istanbul, Turkey.

Yaşar, D., Aksu, A.E., Uslu, O., 2001. Anthropogenic Pollution in İzmit Bay: Heavy Metal Concentrations in Surface Sediments. Turk. J. Engin. Environ. Sci., 25, 299-313.



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