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The Seasonal Variation of Heavy Metals in the Suspended Particulate Material in the Iskenderun Bay (North-eastern Mediterranean Sea, Turkey)

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Özet: ***İskenderun Körfezi'nde (Kuzey Doğu Akdeniz, Türkiye) askıdaki katı maddede ağır metallerin mevsimsel değişimi.*** İskenderun Körfezi'nden Ağustos 2001 ve Temmuz 2002 tarihleri arasında beş istasyondan askıdaki katı maddede kadmiyum, demir, bakır, kurşun, çinko kobalt, krom, alüminyum, mangan ve nikelin dağılımları aylık olarak incelenmiştir. Ağır metal konsantrasyonlarındaki değişimler genel olarak önemli derecede farklı bulunmuştur. Genel olarak körfezin kendini çevreleyen yerleşim bölgelerinden kaynaklanan endüstriyel, tarımsal ve evsel ağır metal kirliliğinden etkilendiği anlaşılmaktadır. Bu sonuçlara göre, ekosistemdeki biyolojik çeşitlilikte göz önüne alınarak, körfezdeki ağır metal kirliliği tehdidini önlemek için, en kısa zamanda koruyucu önlemlerin alınmasının kaçınılmaz olduğu düşünülmektedir.

Anahtar Kelimeler: İskenderun Körfezi, ağır metaller, mevsimsel değişim, askıdaki katı madde.

Abstract: Variations of cadmium, iron, copper, lead, zinc, cobalt, chrome, aluminum, manganese and nickel in the suspended particulate material were examined monthly at five stations in Iskenderun Bay from August 2001 to July 2002. Generally, the variations in concentrations of the heavy metals were found significantly different. The bay has been affected by industrial and agricultural heavy metal pollution from the surrounding facilities and domestic effluents from the cities. According to these results, to prevent this heavy metal pollution threat in Iskenderun Bay, taking into consideration the biodiversity in this ecosystem, it is thought that it is inevitable that protective measurements must be started as soon as possible.

Key Words: İskenderun Bay, heavy metals, seasonal variations, suspended particulate material.

Introduction

The Iskenderun Bay is situated in the eastern-most part of the Mediterranean Sea off southern Turkey (36°C20′N-35°C30′E; 36°C50′N-35°C00′E). Along the coast of the bay, there are many town including, Iskenderun with approximate population of 700.000 to 800.000. The bay is very important for commercial and sport fishing in this region. In this region of the Mediterranean Sea, industries are expanding; most of these industries such as cement factory, textiles, tin, iron and steel factories, aluminum works, batteries factory, wood process, power station, rubbish treatment, food conserves, oil refinery, phosphate loading activities etc. use sea or river systems to dump their sewage. In addition, local practices are not the only potential source of pollution; the predominant current system indicates that pollution from external source is highly possible. Consequently, industrial and urban development in coastal areas exacerbates the marine pollution problem. Wastewater collection and disposal systems have been planned and constructed in some areas, but these are still not sufficient in some other areas due to primarily limited budget.

During the past three decades, the state of the Mediterranean Sea has become a matter of growing international concern. The semi-enclosed nature of this water body, the characteristics of its current system and the increasing population density along its coastline are conductive to water pollution. In order to face this situation, since 1975 a comprehensive pollution prevention and control program sponsored and organized by major United Nations bodies and agencies-the Mediterranean Action Plan-was adopted by the Mediterranean states (WHO 1995). One of the threats to the Mediterranean ecosystem is metal pollution. Raised levels of several trace metals, released into the marine ecosystems by natural and anthropogenic sources, have been reported in different areas of the Mediterranean basin (Cubadda *et al.*, 2001). Intense pollution in the bay has inevitably increased the levels of heavy metals in the water and suspended particulate material. Therefore, it became important to determine the levels of heavy metals in the suspended particulate material (SPM) in order to evaluate the possible risk of fish and other organisms consumption for human health. Although some papers have been published concerning heavy metal levels observed in fish (Kargın, 1996; Türkmen *et al.*, 2004) and shrimps (Kargın *et al.*, 2003) on northern east Mediterranean sea environment, this paper presents preliminary results on the levels of cadmium, iron, copper, chromium, cobalt, zinc, lead, nickel, aluminum and manganese in the SPM from the İskenderun Bay.

Material and Methods

All samples were sampled monthly from the same sites, periods i.e., from August-2001 until July-2002. Figure 1 shows these stations as Arsuz (ARZ), Iskenderun Harbour Area (IHA), İsdemir (İSD), Dörtyol Botaş (DBT) and Petrotrans (PTS). About 180 water samples were taken with polyethylene bottles, filtered through cellulose nitrate filters with pore diameter <0.45 μm, for metal analysis (USEPA, 1979). During 12 months, three samples from each station were taken. Obtained by filtering the water, about 180 filtered materials (suspended particulate matter, SPM) were dried at 100°C to a constant dry weight and stored (Gundacker, 1999). SPM samples were digested with concentrated ultra pure nitric acid in microwave oven (CEM MARS-5) and stored until analysis (Blust *et al.*, 1998). Analysis of metals (Cd, Fe, Cu, Pb, Zn, Co, Cr, Al, Mn, Ni) were carried out using VARIAN SPECTRAA 220 Fast Sequential Flame Atomic Absorption Spectrometry. Analytical blanks were run in the same way as the samples and concentrations were determined using standard solutions prepared in the same acid matrix. Suspensions were duplicated with results as mean values. Results are expressed in mg kg^{-1}. The accuracy and precision of our results were checked by analyzing standard reference material (SRM, Dorm-2). The results indicate good agreement between the certified and analytical values, the recovery of elements being practically complete for most of them. A logarithmic transformation was done on the data to improve normality. One-way analysis of variance (ANOVA) and Duncan's test (p= 0.05) were used to access whether heavy metal concentrations varied significantly between sites and seasons, possibilities less than 0.05 ($p<0.05$) were considered statistically significant. All statistical calculations were performed with SPSS 9.0 for Windows (Özdamar, 1999).

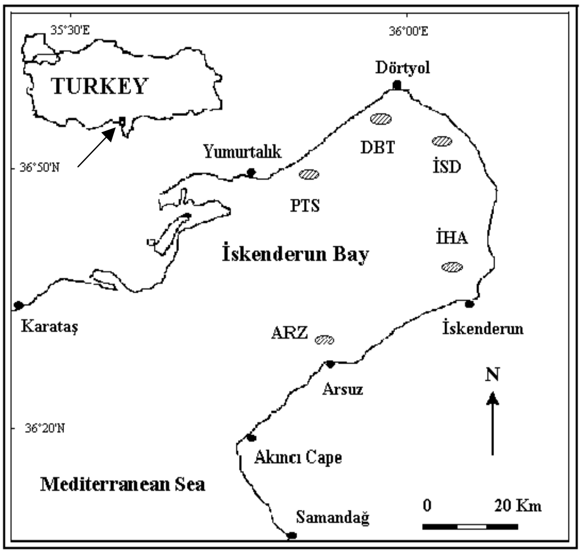

Figure 1. Sampling stations in İskenderun Bay.

Results and Discussion

Seasonal variations at stations of the heavy metal concentrations (HMC's) from Iskenderun Bay were given Table 1 and Figures 2-11. Although the levels of iron, chrome, aluminum, manganese and nickel in summer were higher than those in other months, the levels of cadmium, copper, lead, zinc and cobalt were higher in winter. Results of analysis of variance (ANOVA) indicated that variations among months were statistically significant in all metals ($p<0.05$). It is reported that HMC's may vary by season (Atayeter, 1996; Morley *et al.*, 1997; Akçay *et al.*, 2003; Turgut, 2003).

Table 1. Seasonal distributions of the mean HMC's from İskenderun Bay (N: 15 samples in each months for each metals).

	Mean HMC's with Standard Error (mg kg^{-1} dry wt)*									
	Cd	Fe	Cu	Pb	Zn	Co	Cr	Al	Mn	Ni
Jan	$50.6^{a} \pm 3.6$	$27550^{ab} \pm 3479$	$628^{a} \pm 97$	$783^{a} \pm 108$	$1547^{a} \pm 238$	$202^{a} \pm 28$	$328^{a} \pm 91$	$15726^{ab} \pm 1280$	$619^{ab} \pm 58$	$850^{a} \pm 157$
Feb	$32.7^{b} \pm 2.7$	$27742^{ab} \pm 3249$	$246^{bcd} \pm 34$	$459^{ab} \pm 66$	$1181^{abc} \pm 184$	$122^{bd} \pm 22$	$339^{a} \pm 97$	$21301^{bcd} \pm 2010$	$733^{abc} \pm 92$	$685^{ab} \pm 132$
Mar	$22.2^{bc} \pm 2.2$	$27169^{ab} \pm 3662$	$207^{cd} \pm 29$	$369^{bc} \pm 69$	$1190^{abc} \pm 229$	$70.0^{c} \pm 15$	$316^{a} \pm 56$	$17020^{abc} \pm 1584$	$804^{abc} \pm 127$	$606^{ab} \pm 85$
Apr	$13.5^{de} \pm 1.8$	$25770^{ab} \pm 4426$	$110^{f} \pm 17$	$223^{de} \pm 64$	$1226^{abc} \pm 414$	$21.8^{e} \pm 4$	$262^{a} \pm 48$	$13684^{a} \pm 1086$	$690^{a} \pm 179$	$277^{c} \pm 41$
May	$7.24^{fg} \pm 0.7$	$21894^{a} \pm 2317$	$407^{b} \pm 76$	$65.0^{f} \pm 10$	$593^{de} \pm 79$	$26.3^{e} \pm 5$	$436^{abc} \pm 81$	$21068^{bcd} \pm 2888$	$799^{ab} \pm 182$	$261^{c} \pm 48$
Jun	$8.82^{fg} \pm 1.7$	$22161^{a} \pm 2482$	$286^{bc} \pm 42$	$134^{df} \pm 26$	$535^{e} \pm 132$	$26.8^{e} \pm 6$	$653^{abc} \pm 159$	$23244^{bcd} \pm 2935$	$798^{abc} \pm 138$	$378^{cd} \pm 72$
Jul	$5.88^{f} \pm 0.8$	$24501^{ab} \pm 3022$	$185^{cdef} \pm 30$	$109^{f} \pm 23$	$526^{e} \pm 126$	$77.0^{c} \pm 11$	$697^{bc} \pm 122$	$27747^{d} \pm 3651$	$911^{abc} \pm 184$	$398^{bcd} \pm 56$
Aug	$13.6^{de} \pm 1.5$	$55201^{c} \pm 5216$	$147^{def} \pm 21$	$243^{ce} \pm 42$	$466^{e} \pm 90.2$	$139^{ad} \pm 20$	$1388^{e} \pm 230$	$24387^{cd} \pm 3537$	$1194^{abc} \pm 119$	$915^{e} \pm 131$
Sep	$14.8^{ce} \pm 0.8$	$36537^{b} \pm 4718$	$202^{cd} \pm 33$	$274^{bce} \pm 39$	$662^{bde} \pm 101$	$130^{abd} \pm 19$	$818^{ce} \pm 131$	$21713^{bcd} \pm 1523$	$1009^{abc} \pm 145$	$639^{bde} \pm 147$
Oct	$10.2^{dg} \pm 1.2$	$24164^{ab} \pm 2945$	$307^{bc} \pm 49$	$105^{f} \pm 24$	$814^{bcd} \pm 119$	$56.7^{c} \pm 10$	$665^{abc} \pm 254$	$18666^{abcd} \pm 1168$	$898^{ab} \pm 220$	$440^{cd} \pm 137$
Nov	$33.2^{ce} \pm 6.4$	$28680^{ab} \pm 4163$	$696^{a} \pm 141$	$449^{c} \pm 73$	$1109^{abcd} \pm 197$	$140^{ad} \pm 22$	$597^{abc} \pm 150$	$19335^{abcd} \pm 2611$	$587^{a} \pm 82$	$837^{e} \pm 129$
Dec	$66.7^{a} \pm 3.7$	$26730^{ab} \pm 3691$	$725^{a} \pm 120$	$783^{a} \pm 110$	$1437^{ac} \pm 217$	$199^{a} \pm 28$	$457^{ab} \pm 118$	$16831^{ab} \pm 1866$	$731^{abc} \pm 77$	$844^{e} \pm 146$

* *Within columns, means with the same letter are not statistically significant, p>0.05*

Variations at stations of the HMC's from İskenderun Bay were given in Figure 2-11 and Table 2. Cu, Cr and Ni concentrations at station ARZ, Fe, Pb, Zn and Mn at station İSD, Cd, Co and Al at station PTS were higher than those at other stations. On the other hand, Cd, Pb, Zn and Al concentrations at station ARZ, Co at station İSD, Cu at station DBT, Fe, Cr, Mn and Ni at station PTS were lower than those at other stations. Results of analysis of variance (ANOVA) indicated that variations among stations were statistically significant in all metals except Cd and Co ($p<0.05$). Because of many chrome mines around ARZ region, this metal has high levels at ARZ station. The reason for that the levels of Fe, Pb, Zn, Cd, Co, Al and Mn at stations İDC, DBT and PTS are high may be that many industries such as cement factory, textiles, tin, iron and steel factories, aluminum works, batteries factory, wood process, power station exist coastline at these stations.

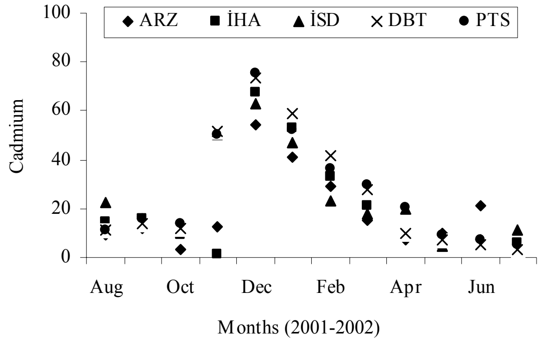

Figure 2. Seasonal variations of the cadmium as mg kg^{-1} dry weight in the SPM from Iskenderun Bay (sampling stations; ARZ, İHA, İSD, DBT and PTS).

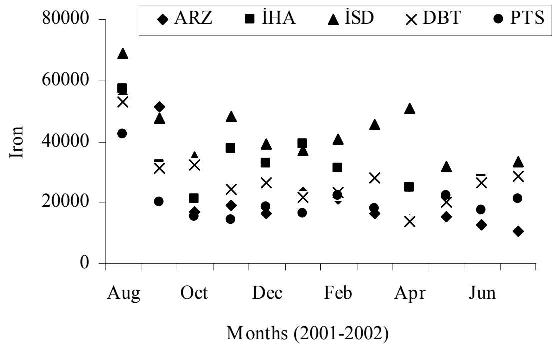

Figure 3. Seasonal variations of the iron as mg kg^{-1} dry weight in the SPM from Iskenderun Bay (sampling stations; ARZ, İHA, İSD, DBT and PTS).

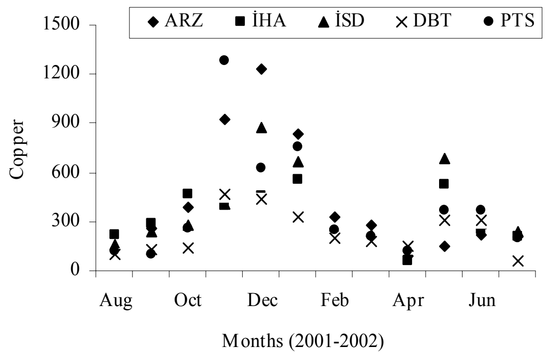

Figure 4. Seasonal variations of the copper as mg kg^{-1} dry weight in the SPM from Iskenderun Bay (sampling stations; ARZ, İHA, İSD, DBT and PTS).

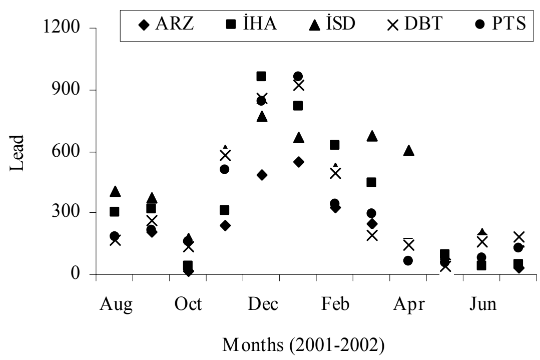

Figure 5. Seasonal variations of the lead as mg kg^{-1} dry weight in the SPM from Iskenderun Bay (sampling stations; ARZ, İHA, İSD, DBT and PTS).

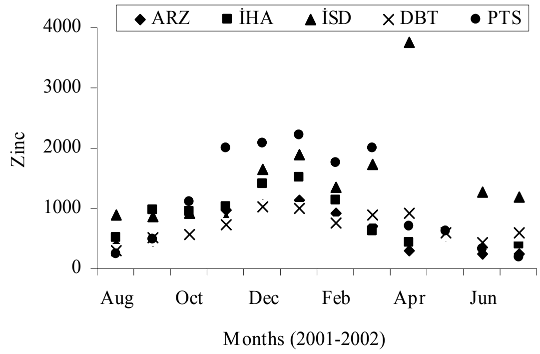

Figure 6. Seasonal variations of the zinc as mg kg^{-1} dry weight in the SPM from Iskenderun Bay (sampling stations; ARZ, İHA, İSD, DBT and PTS).

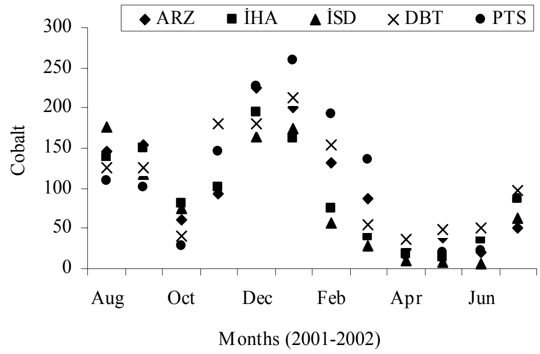

Figure 7. Seasonal variations of the cobalt as mg kg^{-1} dry weight in the SPM from Iskenderun Bay (sampling stations; ARZ, İHA, İSD, DBT and PTS).

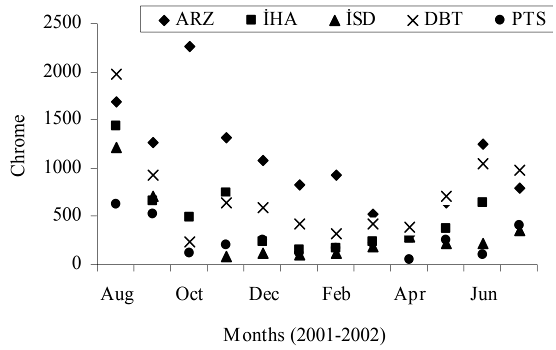

Figure 8. Seasonal variations of the chrome as mg kg^{-1} dry weight in the SPM from Iskenderun Bay (sampling stations; ARZ, İHA, İSD, DBT and PTS).

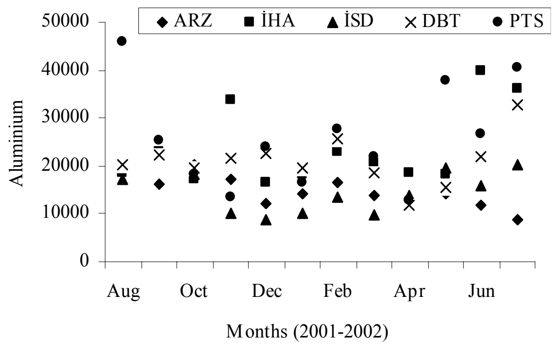

Figure 9. Seasonal variations of the aluminium as mg kg^{-1} dry weight in the SPM from Iskenderun Bay (sampling stations; ARZ, İHA, İSD, DBT and PTS).

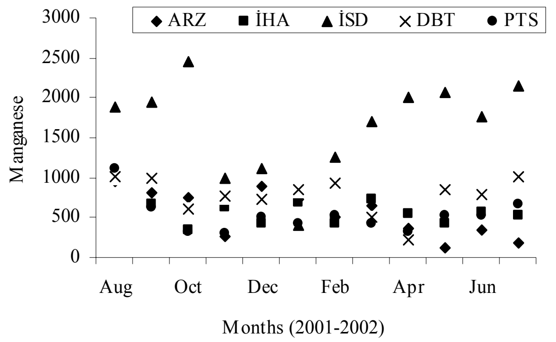

Figure 10. Seasonal variations of the manganese as mg kg^{-1} dry weight in the SPM from Iskenderun Bay (sampling stations; ARZ, İHA, İSD, DBT and PTS).

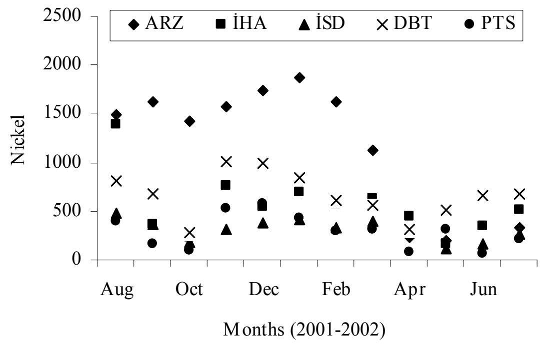

Figure 11. Seasonal variations of the manganese as mg kg^{-1} dry weight in the SPM from Iskenderun Bay (sampling stations; ARZ, İHA, İSD, DBT and PTS).

Table 2. Distribution of the mean HMC's in sampling stations from Iskenderun Bay (N: 36 samples in each stations for each metals).

Site	Mean HMC's with Standard Error (mg kg^{-1} dry wt)*									
	Cd	Fe	Cu	Pb	Zn	Co	Cr	Al	Mn	Ni
ARZ	18.2^{a}± 2.7	22826^{a}± 3190	420^{a}± 72	222^{a}± 35	626^{a}± 76	103^{a}± 16	1074^{a}± 129	14670^{a}± 749	549^{a}± 55	1153^{a}± 111
İHA	20.1^{a}± 3.5	31620^{b}± 2117	317^{ab}± 37	346^{ab}± 63	828^{ab}± 97	91.9^{a}± 14	531^{bc}± 81	23660^{bc}± 1624	584^{a}± 33	554^{b}± 56
İSD	24.7^{a}± 3.2	42082^{c}± 2896	368^{ab}± 52	433^{b}± 55	1411^{c}± 191	88.4^{a}± 15	318^{bd}± 64	14980^{a}± 906	1643^{c}± 103	309^{c}± 26
DBT	26.4^{a}± 4.1	27427^{b}± 2194	233^{b}± 31	344^{ab}± 60	692^{a}± 66	109^{a}± 14	721^{c}± 106	20995^{b}± 1088	774^{b}± 46	663^{b}± 47
PTS	27.1^{a}± 3.8	21087^{a}± 1571	388^{ab}± 72	320^{ab}± 59	1144^{bc}± 171	112^{a}± 18	254^{d}± 38.0	25994^{c}± 2221	523^{a}± 40	291^{c}± 34

**Within columns, means with the same letter are not statistically significant, p>0.05*

Distribution of the HMC's in SPM ranged as follows: Cd: 5.88-66.7, Fe: 21894-55201, Cu: 110-725, Pb: 65.0-783, Zn: 466-1547, Co: 21.8-202, Cr: 262-1388, Al: 15726-27747, Mn: 587-1194 and Ni: 261-915 mg kg^{-1} dry wt respectively. Variations of the HMC's from Changjiang Estuary ranged as Cd: 0.18-0.99, Fe: 47400-56900, Cu: 17.1-65.2, Pb: 12.5-43.3, Zn: 74.2-121.3, Co: 22.9-38.0, Cr: 130.1-190.8, Al: 61400-110100, Mn: 669-1282 and Ni: 21.6-79.1 mg kg^{-1} (Zhang 1999). Belzunce-Segarra et al. (1997) reported that the HMC's from the river Ulla and its estuary (North-west Spain) ranged as Cd: 7.02-27.14, Cr: 21.43-126-4, Cu: 6.84-755.7, Mn: 27.57-5079, Ni: 42.66-130.7, Pb: 20.36-197.8, Zn: 163.7-3380 mg kg^{-1}. The HMC's from the Eolian Basin (South Tyrrhenian Sea) were reported as Cu: 0.7-442, Fe: 93-2405, Mn: 1.3-68.6, Pb: 0.4-72.4 mg kg^{-1} (Rivaro et al., 1998). Morrison et al (2001) reported as Cd: 1.43, Cu: 124.4, Fe: 79200, Mn: 2296, Pb: 5.94, Zn: 188, Al: 107800 mg kg^{-1} from Laucala Bay. When present results were compared with other findings, the levels of Cd, Co, Cr, Cu (except Ulla river estuary), Fe and Mn (in only Eolian basin), Ni, Pb, Zn (in only Changjiang bay) were higher than other areas compared. On the other hand, the levels of Mn and Zn in the river Ulla and its estuary, Fe, Mn and Al in the Laucala Bay, Fe and Al in the Changjiang Estuary were higher than our results.

Heavy metal concentrations in the suspended particulate material from Iskenderun Bay were monitored during August 2001-July 2002. They showed seasonal and spatial variations. In general, although the levels of Cd, Pb, Cu, Zn and Co were generally high in winter, Fe, Cr, Mn and Al were high in August and September. On the other hand, although the levels of Cr and Ni were maximum in station ARZ and decreased towards other ones, other metals were minimum at station ARZ and increased towards other ones. As seen, results of the present study are generally higher except some metals than those of open literature. This situation may show that Iskenderun Bay has been considerably affected from the sources of pollution. According to these results, in the near future, to prevent this heavy metal pollution threat in Iskenderun Bay, taking into consideration the biodiversity in this ecosystem, it is thought that it is inevitable that protective measurements must be started as soon as possible.

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