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Accumulation and Distribution of Total Chromium in Seawater, Sediment and Some Organisms and Its Behaviour Processes in Izmir Bay (Aegean Sea)

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Özet: İzmir Körfezinde Su, Sediment ve Bazı Organizmalardaki Total Krom Birikimi, Dağılımı ve Onun Davranış İşlevleri. Aralık-1989 ve Aralık 1990 arasında, İzmir Körfezi'nde belirlenen 11 istasyonda dip suyu, yüzey sedimenti ve *Solea vulgaris* Quensel (1806), *Buglossidium luteum* Risso (1810), *Arnoglossus laterna* Walbaum (1792), *Gobius niger* Linnaeus (1758) gibi bazı organizmalarda total Krom konsantrasyon düzeyleri ölçülmüş ve Kromun bu ortamdaki davranışı araştırılmıştır. Mevcut çalışma göstermiştir ki, İzmir Körfezi sedimentinde kuvvetli bir Cr_{tot} zenginleşmesi vardır. Deniz suyundan Kromu adsorbe edebilen yüksek organik ve inorganik asılı maddelerin hızlı çökelmesi krom konsantrasyonunun deniz suyunda çok düşük düzeylerde kalmasına neden olurken, sedimentin Krom içeriğinde hızlı bir yükselmeye sebep olmuştur. Cr_{tot} konsantrasyonu, deniz suyu ve sedimentinde sırasıyla 4.1 - 13.6 µg l^{-1} ve 24 - 967 mg kg^{-1} kuru ağırlık arasında bir değişim göstermiştir. *S. vulgaris, B. luteum, A. laterna* ve *G. niger* gibi bazı bentik organizmaların kas dokularındaki Cr_{tot} konsantrasyonları da, sırasıyla, 127.7 - 663.3, 157.3 - 1021.9, 176.9 - 1215.0 ve 132.2 - 1493.0 µg kg^{-1} wet wt arasında değişim göstermiştir. Yukarıda adı geçen türlerin biokonsantrasyon faktörleri (BCF) de, sırasıyla, 550, 503, 708, 627 olarak hesaplanmıştır. Bu araştırmada, ayrıca, diğer organizmaların Cr_{tot} konsantrasyon ve BCF değerleri de verilmiştir.

Anahtar Kelimeler: İzmir körfezi, kirlilik, total krom, deniz suyu, yüzey-sediment, balık kas dokusu

Abstract: The concentrations of total chromium (Cr_{tot}) were measured in deep-water (DW), surface sediment (SS) and some organisms such as *Solea vulgaris* Quensel (1806), *Buglossidium luteum* Risso (1810), *Arnoglossus laterna* Walbaum (1792), *Gobius niger* Linnaeus (1758) obtained from 11 sampling stations in Izmir Bay and its behaviour in this environment has been studied between December 1989 and December 1990. The present study showed that, there is a strong enrichment of Cr in the sediment of Izmir Bay. Precipitation processes of high organic and inorganic suspended matter which may adsorbe chromium from sea water; give rise to high chromium level in the sediment and low chromium concentration in sea water. The Cr_{tot} concentration in sea water and sediment were ranged between 4.1 - 13.6 µg l^{-1} and 24 - 967 mg kg^{-1} dry weight, respectively. Cr_{tot} concentration in the tissues of *S. vulgaris, B. luteum, A. laterna* and *G. niger* ranged between 127.7 and 663.3, 157.3 and 1021.9, 176.9 and 1215.0, 132.2 and 1493.0 µg kg^{-1} wet wt., respectively. Bioconcentration factors (BCF) of *S. vulgaris, B. luteum, A. laterna and G. niger* were 550, 503, 708 and 627, respectively. In this study, Cr_{tot} levels and BCF of other organisms have been also presented.

Keywords: Izmir Bay, pollution, total chromium, sea-water, surface-sediment, muscle of fish

Introduction

Development of technology and improvement of industry may cause the environmental pollution problems (Clark, 1992). The discharge and dumping of sewage and industrial spoils released significant quantities of heavy metals in Izmir Bay. Some of these industries such as paper, printing, plastics, iron-steel, textile, leather and food are located around Izmir Bay. It is well known that the sources of Cr in aquatic environment are such industries (IRPTC, 1978).

Chromium (Cr) is an abundant element in the earth crust and occurs in oxidation states ranging from Cr^{+2} to Cr^{+6}. The most common form in nature is Cr^{+3}, which is also the valence which is considered essential as a trace element in many aquatic organisms (Rainbow, 1988). Although Cr is known to be essential for the growth, it may be potentially toxic to living organisms (Bryan, 1976; Rainbow, 1985, 1993, 1995). Of the two stable Cr forms as to valence, hexavalent Cr (Cr^{+6}) is more toxic than the trivalent form (Cr^{+3}) (Hayes, 1982; Tandon, 1982; Suzuki, 1984 and Horitsu, 1987).

Marine organisms, especially fish accumulate heavy metals including chromium in their tissues and organs in higher quantities than those found in the ambient sea water (El Sokkary, 1980 and Morales, 1980). The quantity of heavy metals accumulated depends on the age, habitat and feeding behaviour of the fish (Uysal, 1980, 1982).

Sea water concentrations of Cr ranges from 0 - 0.36 ppb, mostly as hexavalent Cr. The trivalent form also exists in water but it may eventually precipitate or be absorbed. Seawater samples from the western Mediterranean contained Cr concentrations (tri-and hexevalent) in the range of 0.39 - 0.41 $\mu g\ l^{-1}$ (Bernhard and Zattera, 1975).

In seawater, Cr is complicated by the occurrence of reduced (III), oxidised (VI) and possibly organic species (Elderfield, 1970, Nakayama *et al*., 1981). Whereas Cr^{+6} is highly soluble, Cr^{+3} has greater particle reactivity and seems to be readily scavenged from the water column. Most reliable data, in agreement with thermodynamic calculations (Elderfield, 1970), indicate that Cr^{+3} concentration is low in the open ocean (Murray, 1983) and in coastal waters (Cranston and Murray, 1978). However, there is convincing evidence that in coastal waters (Jandel and Minster, 1984) and near continental margins (Murray, 1983), Cr^{+3} concentration is not as low as expected and may be subtained by biological activity or release from sediments.

Surface variations of Cr_{tot} concentrations in seawater are small but, in bottom waters, a slight increase in concentration is generally observed which might be explained by a release from sediments (Murray, 1983, Jandel and Minster, 1984).

Distribution of available trace element in sediment depended on the mineralogical

composition. However, Cr concentration in sediment samples from coastal areas is higher because of terrestrial water flowing from river to these areas (Jandel and Minster, 1984, Balcı and Türkoğlu, 1993).

In order to understand behaviour processes of the Cr, total Cr were analysed in deep-water, surface sediment and some benthic organisms such as *Solea vulgaris*, *Buglossidium luteum*, *Arnoglossus laterna*, *Gobius niger* collected from 11 sampling stations in Izmir Bay, between December 1989 and December 1990.

Materials and methods

Izmir Bay (Fig 1.) is located in the eastern part of the Aegean sea, Turkey, lying between latitudes 38^{o} 20' and 38^{o} 42' and longitudes 26^{o} 25' and 27^{o} 10'. A part of Izmir city and several industries are located in the Inner Bay. Untreated or partially treated industrial and domestic waste-waters are discharged directly or carried by several streams into the Bay. Izmir, with a population of over 2.0 million is one of the fastest growing cities in Turkey. The main sources of pollution in Izmir Bay are domestic and industrial wastes, rainfall and associated pollutants from run off, shipping and agricultural sources.

Fig 1. Sampling stations in the Izmir Bay, Turkey

From the topographic and hydrographic points of view, the Bay is divided into inner, middle and outer regions. Its average depth is about 20-25 m. The inner Bay, which is shallower, reaches a maximum depth of about 20 m and exhibits a limited water exchange

with the outer Bay. Both the part area and the central part of the Inner Bay are dredged to improve navigation. Pollution by nutrients is a problem, and red-tide occurrences are reported to have increased in frequency in recent years (Kocataş *et al*., 1988).

Between December 1989 and December 1990, Cr_{tot} content of surface sediment, deep-water and in the tissues of some organisms collected from 11 sampling stations in Izmir Bay (Fig.1) by "R/V K.Piri Reis" were investigated considering with the behaviour processes of Cr_{tot} in marine environment.

Seawater samples were taken from sediment-water interface (0.5-1 m) by Nansen bottle (1.8 litter) precleaned with clean seawater-distilled hydrochloric acid (40 %). 250 ml or 500 ml of unfiltered sea water were immediately drawn in two polypropylene bottles, precleaned with two successive washes with 0.1 N distilled hydrochloric acid. In the laboratory, samples were analysed for total chromium concentration using "Solvent extraction technique using APDC - Chloroform" by flame Atomic Absorption Spectrometry (Kinrade and Van Loon 1974). 100 ml of seawater was taken as a subsample, the pH was adjusted to 2.5 and 1.25 ml of 2 % APDC, plus, 10 ml of 90 % chloroform were added. The solution was extracted for 20 minute and the concentration of Cr_{tot} in the organic layer was measured.

Surface sediments were collected using a "van-veen grab" which takes sample from depth of 100 m. and stored in clear polyethylene bags. In the laboratory, they were dried at 80 ^{o}C for 24 hours and 1 gr. of dried sample wet-digested in Teflon flask using concentrated HNO_3 : $HClO_4$ (5:1) (Sinex *et al*., 1980). The acid extracts were filtered and made up to a fixed volume, and placed in acid-washed polyethylene bottles.

Biological samples were catched using a "Beam-trawl" and stored in clean polyethylene bags like sediment samples. After sampling, flesh samples (subsamples) were dissected. The subsamples were digested with HNO_3 : $HClO_4$ (5:1) (Bernhard, 1976).

All samples were transported to the laboratory and kept in a deepfreezer (-21^{o}C) until analysis.

Cr_{tot} contents of all samples were determined using a pye-unicam model spq. AAS with flame technique supported by acetilene-NO_2 fuel (NAS, 1974).

Bioconcentration factor (BCF) of organisms were calculated as a proportion between chromium accumulation value of organisms and concentration of seawater.

The accuracy of the method was established using reference material, from the international Atomic Energy Agency Laboratory in Monaco, coded SD-N-1/2. Cr values found in this study were in good agreement with those cited in the literature.

Results and discussion

Chromium Concentrations in Deep-Water and Surface Sediment

The average data on seasonal and annual variations of Cr concentrations of DW and SS at different stations in Izmir Bay are listed in Table 1. In different regions in the Izmir Bay (Inner, Middle and Outer Bay), the seasonal and annual variations of them calculated from these data are listed in Table 2.

Table 1. Seasonal and annual variations of Cr_{tot} concentrations in deep-water (DW) and surface-sediment (SS) at different stations in Izmir Bay (DW: µg l^{-1}; SS: mg kg^{-1} dry weight).

		SPRING		SUMMER		AUTUMN		WINTER		ANNUAL VARIATIONS			
St. no	Depth (m)	DW	SS	DW	SS	DW	SS	DW	SS	N	DW	N	SS
1	9	7.3	846	6.5	239	8.2	458	8.2	360	10	7.5	10	476
2	12	6.8	465	6.3	441	4.8	429	7.9	363	10	6.4	10	424
3	14	13.0	187	5.7	252	6.1	140	5.8	195	10	7.6	10	193
4	17	5.9	101	5.7	86	7.0	82	8.2	77	10	6.7	10	86
5	28	4.5	77	5.7	86	7.0	82	4.9	83	10	5.5	10	82
6	28	5.8	78	8.2	88	5.9	86	5.8	74	10	6.4	10	81
7	28	5.4	82	5.4	86	6.7	85	9.6	87	8	6.8	8	85
8	31	5.4	84	8.2	89	8.5	87	11.9	88	10	8.5	10	87
9	67	7.9	65	7.7	67	7.5	53	7.9	62	4	7.7	4	63
10	31	7.3	28	6.9	27	7.6	26	6.1	27	6	7.0	6	26
11	28	6.6	23	6.5	27	6.6	24	6.3	28	6	6.5	6	25
M	27	6.9	185	6.6	135	6.9	141	7.5	131	94	7.0	94	148

N: Number of samples, M: Average of Cr_{tot}

The annual variation of the Cr_{tot} concentrations in sediment ranged between 25 and 476 mg kg^{-1} dry weight (Tab.1). It appears in Table 2 that Inner Bay has the greatest Cr_{tot} content with 967 mg kg^{-1} dry wt. Literature review showed that Cr_{tot} concentrations in sediment increased gradually from September 1986 (110 mg kg^{-1} dry wt. in Inner Bay) to September 1990 (265 mg kg^{-1} dry wt.) (Alyanak, 1986, Uslu *et al*., 1990). It may be concluded that Cr_{tot} input to inner Bay is a continuous problem.

The Chromium concentrations at stations 10 and 11 (see Tab.1) (26 and 25 mg Cr_{tot} kg^{-1} dry wt. respectively) in the outer Bay can be considered to reflect background levels of chromium. These values are in full conformity with values obtained in previous studies (Türkoğlu *et al*., 1992; Balcı and Türkoğlu, 1993).

Table 2. Seasonal and annual variations of Cr_{tot} concentrations in deep water and surface sediment in different region in Izmir Bay, Turkey (DW: µg l^{-1}, SS: mg kg^{-1} dry weight).

				SPRING		SUMMER		AUTUMN		WINTER		ANN. VAR.	
AREAS	St. no	N		DW	SS	DW	SS	DW	SS	DW	SS	DW	SS
			Min.	4.5	75	4.6	85	4.1	80	4.5	62		
INNER			M	7.5±	335±	6.0±	254±	6.5±	277±	7.0±	233±	6.7±	275±
BAY	1-5	50		0.98	97.7	0.12	44.2	0.38	57.0	0.51	42.5	0.38	59.7
			Max	13.0	967	7.1	453	8.2	487	8.2	426		
	6		Min.	5.4	21	5.4	27	5.4	77	5.4	28		
MIDDLE			M	5.9±	61±	7.3±	58±	5.9±	86±	7.2±	55±	6.5±	72±
BAY	7	24		0.18	9.93	0.42	10.4	0.13	10.7	0.84	9.34	0.36	9.95
	11		Max	7.7	84	8.2	88	6.8	96	12.3	95		
	8		Min.	5.4	28	6.8	27	7.1	26	5.4	24		
OUTER			M	6.6±	59±	8.2±	61±	8.4±	55±	8.6±	58±	7.8±	64±
BAY	9	20		0.39	8.58	0.20	9.47	0.17	9.2	0.89	9.22	0.33	9.25
	10		Max	8.2	84	9.6	89	9.7	87	13.6	88		

N: Number of samples, Min: minimum of Cr_{tot}, DW: Deep-water, M: Average of Cr_{tot}, Max: maximum of Cr_{tot}, SS: Surface Sediment
Note: Each value represents the mean of two replicates.

By comparison with published data from other Mediterranean coasts (Voutsinou, 1982; Whitehead *et al*., 1986), the chromium concentrations reported here for the inner Bay were indicative of a polluted environment. Further monitoring would appear to be required to established the temporal trends in sediment contamination as a development of the area continues.

Cr_{tot} levels in seawater of Izmir Bay ranged between 4.5 and 13.0 µg l^{-1} and showed seasonal and regional changes (Tab. 1 and 2). In spring and winter, Cr concentration of seawater were more higher in inner Bay than other seasons and regions. It may be caused to take industrial and domestic waste-waters coming from several stream into the inner Bay, due to heavy rainfall in Spring and Winter. In Winter, reason of high Cr concentration in Station 8 (11.9 µg l^{-1}) (See Tab.1) is due to waste-waters including chromium coming from Gediz river which is placed on industrial establishments such as textile and leather. These values were more higher than background levels of the Mediterranean Sea (Jaendel and Minster, 1987). On the other hand, these average Cr_{tot} levels were comparable with values obtained in the Gulf of Gera (Greece) (6.6 µg l^{-1}) (Scoullos et al., 1982).

The average values in Tables 1 and 2 show that Cr_{tot} concentrations of surface sediment in the inner area of Izmir Bay have been much more higher than the other polluted coastal

areas of Mediterranean such as Fos (France), 20 ppm; Barcelona (Spain) 25 ppm; Almeria (Spain), 3 ppm; Bougie (Algeria) 11 ppm; Sulina (Romania) 13 ppm; Dubrovnik (Yugoslogia) 41 ppm; Geneva (Italy) 40 ppm (Whitehead *et al*., 1986). However, average Cr_{tot} concentrations in surface sediment of Izmir Bay with 148 mg Cr_{tot} kg^{-1} dry wt. was lower than those obtained (165 mg $Cr_{tot\ Kg}^{-1}$ dry w.) in Termaikos Gulf (Greece) (Voutsinou-Taliadouri, 1982).

In the present study, there were strong enrichment of Cr_{tot} in sediments of Izmir Bay. Precipitation processes of high organic and inorganic suspended matter which may adsorbe chromium from sea-water, give rise to chromium content of sediment while chromium concentrations of sea-water, though chromium doesn't form a sulphide in seawater, H_2S in the ocean will reduce chromium to the trivalent form, which precipitates as the hydroxide (Krouskopf, 1956). All of these mechanisms may be responsible for the low levels of chromium which occur in the seawater of Izmir Bay (Tables 1 and 2), due to it was considerably high organic-inorganic suspended matters and H_2S contents of the Inner Bay (Uysal, 1978a).

Cr_{tot} concentrations in the some organisms

The data on the average length, weight of some organisms with standard deviations (SD) and minimum and maximum values of Cr_{tot} concentrations and number of samples and bioaccumulation factors of these organisms in Izmir Bay are given Table 3. The data on the annual variations of average Cr_{tot} concentrations in some demersal fishes catched from sampling stations of izmir Bay are shown in Fig.2. Annual variations calculated from these data of Cr_{tot} concentrations are illustrated depending on region of Izmir Bay in Fig. 3.

Average Cr_{tot} concentrations in the tissue of 20 demersal and semi demersal fish and *P. kerathurus* were determined. Average Cr_{tot} concentrations in Table 3. show that there are different accumulation levels of Cr_{tot} in the different species. This is probably due to differences in their biotop and feeding habitats and biologies. Data in Table 3 also show the high concentrations of Cr_{tot} in the muscle of fish catched from Izmir Bay. Some of the species such as *S. vulgaris, S. alcedo, D. annularis, D. vulgaris, C. conger* and *P. kerathurus* are consumed by the people living in this area. However, the fish consumption in Izmir is generally low though fishermen may consume high amounts in some areas.

Table 3. Average Cr_{tot} concentrations in some organisms from Izmir Bay (µg kg^{-1} wet-weight)

Species	N	TL (cm)	TW (g)	M	Min.	Max.	BCF
Solea vulgaris Quensel (1806)	16	18.3±4.8	74.6±4.3	384.8	127.7	663.3	550
Buglessidium luteum Risso (1810)	60	8.8±0.6	7.4±2.1	351.9	157.3	1021.9	503
Arnoglossus laterna (Walbaum, 1792)	80	9.9±1.9	9.0±6.6	495.9	176.9	1215.0	708
Gobius niger (Linnaeus, 1758)	58	11.2±1.7	17.3±3.0	439.0	132.2	1493.0	627
Serranus hepatus (Linnaeus, 1758)	20	8.6±0.8	11.1±3.4	560.1	279.0	1046.2	800
Serranus scriba (Linnaeus, 1758)	4	16.0±0.9	57.7±5.6	219.0	181.3	255.2	312
Serranus cabrilla (Linnaeus, 1758)	6	14.0±0.7	40.4±4.9	367.5	317.5	412.4	525
Diplodus vulgaris (Geoffroy saint-Hilaire,1817)	8	12.3±1.6	30.9±12.7	259.0	202.6	315.3	370
Diplodus annularis (Linnaeus, 1758)	8	11.9±2.1	31.0±9.2	382.4	218.0	681.6	546
Smaris alcedo (Linnaeus, 1758)	24	13.3±2.2	28.2±10.7	210.9	106.8	264.3	302
Boops boops (Linnaeus, 1758)	12	16.1±1.8	48.1±8.2	298.0	207.5	340.1	428
Bothus podas (delaroche, 1809)	6	14.8±0.6	39.3±3.3	155.8	112.4	199.3	223
Pagrus pagrus (Linnaeus, 1758)	6	11.0±1.5	18.2±6.4	230.9	195.6	266.2	330
Pagellus erithrynus (Linnaeus, 1758)	6	11.1±0.5	16.8±1.7	200.0	156.2	243.8	286
Pagellus acerna (Risso, 1826)	4	14.0±2.4	36.3±3.2	297.4	227.2	342.4	430
Merluccius merluccius (Linnaeus, 1758)	6	22.1±3.9	90.1±50.1	284.5	149.8	511.2	406
Conger conger (Linnaeus, 1758)	4	37.0±4.9	70.2±19.7	289.5	251.7	332.9	412
Trachurus trachurus (Linnaeus, 1758)	4	18.0±1.8	51.1±4.6	141.3	123.4	156.6	202
Trigla lineata (Linnaeus, 1758)	6	18.8±2.0	80.0±28.2	179.4	123.2	239.3	256
Symphodus tinca (Linnaeus, 1758)	4	12.5±0.9	23.2±5.3	234.1	198.8	270.4	334
Penaus kerathurus (Forskal.)	15	15.3±2.3	26.7±3.4	736.2	698.2	774.2	1052

N: number of samples, TL: total length of organisms (cm), TW: total weight of organisms (gr.), Min: minimum value of Cr_{tot}, Max: maximum value of Cr_{tot}, BCF: bio-concentration factor, M: average value of Cr_{tot}
Note: Each value represents the mean of two replicates.

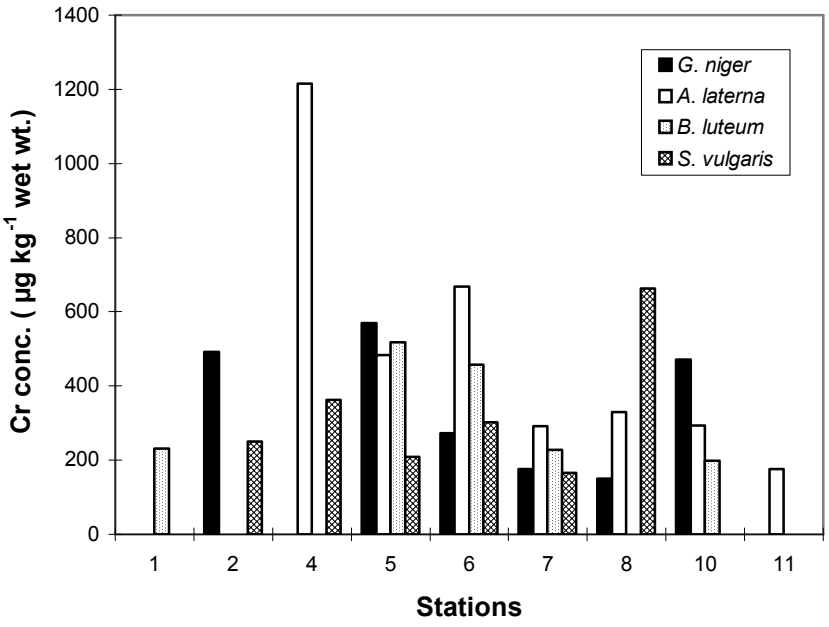


Fig.2. Average Cr_{tot} concentrations in some demersal fish at different stations in Izmir Bay.

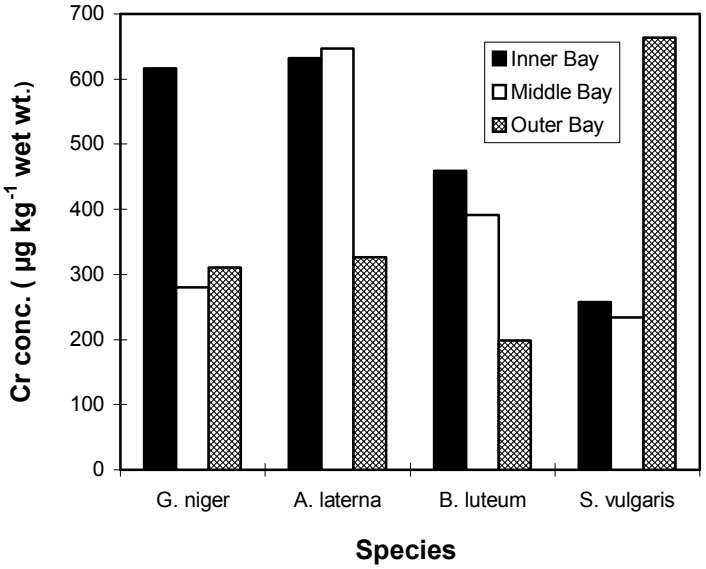


Fig.3. Average Cr_{tot} concentrations in some demersal fish in different regions in Izmir Bay.

Fig.3 shows that there is a decrease in Cr_{tot} concentrations of fish species from inner to outer Bay, except, *S.vulgaris* that had a maximum value of 663.3 µg Cr_{tot} kg^{-1} wet wt. in the outer bay (St. 8) while a low value in the inner Bay (250.4 µg Cr_{tot} kg^{-1} wet wt.) (Figs 2 and 3).

The distribution of Cr_{tot} concentrations of the fish species in different regions (inner, middle and outer Bay) is a expecting result, due to, Cr_{tot} values of the species were paralleled with Cr_{tot} value of surface sediment samples (Tab.2). However, in the present study, Cr_{tot} value of *S. vulgaris* (384.8 µg kg^{-1} wet wt.) and *P. kerathurus* (736.2 µg kg^{-1} wet wt.) are similar to those other studies, in last decade (Uysal 1978b, 1980, 1982).

Also, *D. annularis, S. alcedo, P. acerna* and *S. scriba* had 382.4, 210.9, 297.4, 219.0 µg kg^{-1} wet wt., respectively. These values were comparable to those obtained from the demersal fish samples in Gera Bay (Greece) such as 435 µg kg^{-1} wet wt. for *D. annularis*, but some of them were quite low (such as *S. scriba* 35, *S. alcedo* 53, *P. acerna* 120 µg kg^{-1} wet wt.) (Grimanis et al., 1980).

It was demonstrated that the fish accumulated chromium in their tissues in higher quantities compared to those found in the ambient sea water (Average, 7.0 µg l^{-1}) (Tab.1). These results about bioaccumulation of the fishes are presented as bioconcentration factor (BCF) in Table 3.

According to the results, *P. kerathurus* had a maximum concentration factor (BCF:1052) while *T. trachurus* had a minimum concentration factor (BCF:202). These values are in full conformity with literature (El Sokkary, 1980; Morales, 1980; Uysal, 1980).

As a result, it can be said that Izmir Bay which is polluted with industrial and domestic waste-waters coming from terrastial sources by four creek (Melez, Arab, Manda, Bornova) and a river (Gediz) is also considerably polluted with chromium, due to, textile leather and tinning industries in Izmir. Therefore, there is a need for investigation in to the less mobile benthic fish, from the point of view of human health. In addition to these, studies should be continued in order to monitor uptake and accumulation levels of other metals, like a chromium.

Also, it should be continued studies which on heavy metal analyses of sediment and seawater due to chromium in sea water is accumulated as a biological and precipitated to the sediment with several liqument or accumulated of chromium in organism can return to the sediment.

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