Bull. Environ. Contam. Toxicol. (1999) 63:673-681

Bulletin of Environmental Contamination and Toxicology

Heavy Metal Concentrations in Fish Tissues from the Northeast Mediterranean Sea

M. Kalay,[1] Ö. Ay,[1] M. Canli[2]

[1] University of Mersin, Faculty of Aquaculture, Çiftlikköy, Mersin, Turkey
[2] University of Çukurova, Faculty of Arts and Sciences, Department of Biology, Balcali 01330, Adana, Turkey

Received: 16 February 1999/Accepted: 19 August 1999

Some of the marine environment world-wide have been contaminated by heavy metals and as a result of this animals living in contaminated waters showed high metal concentrations (Mance, 1987; Langston, 1990; Merian, 1991; Bryan and Langston, 1992).

Over a few decades there has been growing interest to determine heavy metal levels in the marine environments and attention was drawn to find out contamination level of public food supplies particularly fish. Therefore, the marine environments are occasionally monitored for heavy metal contamination in water, sediment and animals. It is well known that heavy metals accumulate in tissues of aquatic animals and therefore heavy metals measured in tissues of aquatic animals can reflect the past exposures. Tissue concentrations of heavy metals can also be a reasonable measurement for public health standards and for animals' health point of view.

The aim of this study is to determine heavy metal (Cd, Pb, Cu, Cr, Ni, Zn and Fe) concentrations in the muscle, gill and liver of fishes *(Mugil cephalus, Mullus barbatus, Caranx crysos)* from three stations (Mersin, Karataş and Iskenderun Bay) in the north-east Mediterranean Sea. These areas are industrial and agricultural regions of Turkey and receive many untreated waste waters by direct inputs and inputs via rivers. Iskenderun is an industrialised city containing a big steel plant (station 1). Mersin is also an industrialised city with 500,000 population (station 3). These two cities also contain big harbours. However, Karataş a little town and does not have many industrial plants in its vicinity (station 2). The animals chosen here are very important food supplies for Mediterranean Peoples and also represent different ecological habitats and different feeding behaviours. Thus, this study was conducted to determine the levels of heavy metal distribution among tissues from various animals, Also it was intended to investigate the potential for an overload of heavy metals in the food chain of humans.

MATERIALS AND METHODS

The grey mullet *Mugil cephalus* (26.9±2.53 cm and 182±49.2 g), red mullet *Mullus barbatus* (17.7±1.01 cm and 78.4±12.4 g) and blue runner *Caranx crysos* (21.1±1.31 cm and 85.7±9.69 g) used in this study were sampled at 3 stations from the northeast Mediterranean in November 1996. The animals were purchased from local fishermen on the spot as soon as their fishing boats landed. The animals were packed in ice and brought to the laboratory on the same day. In the laboratory, they were immediately dissected with clean equipment. Total size and weight of the animals were measured. There was no

Correspondence to: M. Kalay

significant difference regarding the size and weight of the animals among stations (P>0.05), since size may be an important factor in heavy metal accumulation of aquatic animals (Canli and Furness, 1993a and b).

Twenty fish were obtained from each station and they were brought to the laboratory on ice in the same day of capture. The gill, liver and muscle tissues of the animals were dissected using clean equipment and put in petri dishes. Tissues of the same species from the same station were pooled to make 5 subsamples and pooled tissues were transferred to an oven set to 120 °C to dry. Drying continued until all the wet tissues reached to a constant weight, Dry tissue samples were put into digestion flasks and 4 ml perchloric acid and 8 ml nitric acid (Merck) were added. The digestion flasks were then put on a hot plate set to 120 °C (gradually increased) until all the materials were dissolved. After digestion the digested samples were diluted with distilled water appropriately in the range of standards which were prepared from stock standard solution of the metals (Merck). Metal concentrations in the samples were measured using a Perkin Elmer AS 3100 flame atomic absorption spectrophotometer. Metal concentration in a tissue was presented as µg metal/g dry weight. Accuracy of the instrument during each measurement was checked by two samples of reference material (TORT 1 lobster hepatopancreas, National Research Council, Canada). Mean values and standard deviations of reference material measured in this study were within 10% ranges of the reference values. Statistical Analysis of data was carried out using SPSS statistical package programs. Kruskall-Wallis one way Anova was used to compare data among stations (Ay et al. 1999).

RESULTS AND DISCUSSION

Mean concentrations and associated standard deviations of cadmium, lead, copper, chromium, nickel, zinc and iron in the gill, liver and muscle of *Mugil cephalus, Mullus barbatus* and *Caranx crysos* collected from 3 stations in the north-east Mediterranean Sea are given in Tables l-7. Results of statistical comparisons of tissue metal concentrations among 3 stations are also given in these tables.

Cadmium concentrations in the tissues of the animals were elevated and highest cadmium concentrations were found in the gill and liver. Cadmium levels in grey mullets did not vary significantly between stations, however, there were some variations in other species. Similarly, lead concentrations also did not vary significantly among stations except in *Caranx crysos*. Station 1 showed highest lead concentrations in the tissues of all the animals and the gills showed highest levels, while the muscle showed the lowest (Table 2). Station 1 is located off a city called Iskenderun which has many factories including a steel plant. High lead concentration in this station may be due to untreated effluents coming from these sources. Copper concentrations in some tissues of *Caranx crysos* varied significantly among stations, but not in the other species. Copper concentrations in the liver of *Mugil cephalus* were much higher than in the liver of the other fishes from all the stations (Table 3). Chromium concentrations in the tissues of the animals were also found to be elevated and generally highest concentrations were in the gills and followed by the liver and muscle (Table 4). Except the grey mullets, chromium concentrations in some tissues of the animals showed significant differences among station. Nickel concentrations were also elevated in all the tissues, the gill tissues showing the highest concentrations. Nickel concentrations in the tissues were significantly different among stations, except in the tissues of red mullets (Table 5). Zinc and iron with naturally high concentrations in fish tissues also varied among stations, except iron concentrations in *Mugil Cephalus* (Table 6 and 7).

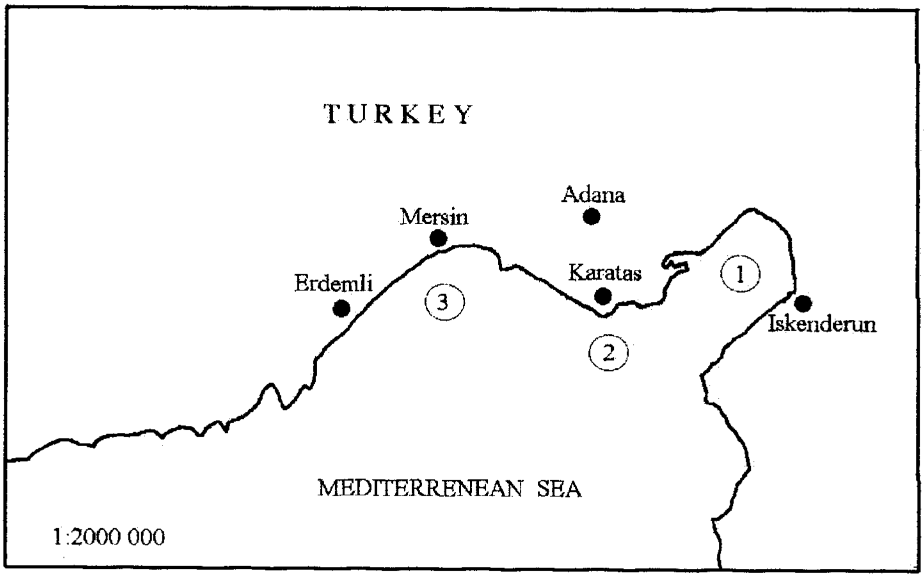

Figure 1. A map of the north-east Mediterrenean sea. Numbered circles indicate approximate sampling stations of animals.

Table 1. Mean concentrations (µg metal/g d.w.) and associated standard deviations of cadmium in the gill, liver and muscle of fishes *Mullus barbatus* (MB), *Caranx crysos* (CC) and *Mugil cephalus* (MC) caught from three stations in the north-east Mediterrenean Sea. Results of statistical differences (P value) among three stations are also given in these tables. NS=not significant (P>0.05)

Station	Gill	Liver	Muscle
MB 1	2.25±0.50	1.98±0.49	1.43±0.97
2	3.70±0.95	1.63±0.25	1.03±0.13
3	2.79±0.38	2.12±1.27	1.07±0.06
P Value	0.017	NS	NS
CC 1	2.64±0.40	5.93±1.14	1.23±0.23
2	3.34±0.81	2.30±0.49	1.36±0.20
3	2.76±0.40	0.84±0.46	0.61±0.16
P Value	NS	0.002	0.01
MC 1	2.36±0.27	3.61±1.65	1.07±0.30
2	2.30±0.40	1.29±0.10	0.86±0.07
3	2.19±0.41	2.26±0.38	0.96±0.44
P Value	NS	NS	NS

Table 2. Mean concentrations (µg metal/g d.w.) and associated standard deviations of lead in the gill, liver and muscle of fishes *Mullus barbatus* (MB), *Caranx crysos* (CC) and *Mugi1 cephalus* (MC). See Table 1 for details.

Station	Gill	Liver	Muscle
MB 1	15.61±3.94	8.42±1.90	9.11±6.05
2	22.35±4.66	6.10±1.17	5.34±1.12
3	20.22±1.77	9.28±5.39	5.94±3.41
P Value	NS	NS	NS
CC 1	17.51±1.59	15.72±2.86	7.50±1.69
2	20.11±5.64	8.68±2.94	6.36±1.83
3	18.24±0.97	4.73±2.74	4.43±1.40
P Value	NS	0.004	0.046
MC 1	21.13±3.30	11.21±5.93	7.33±2.11
2	21.23±8.03	6.13±1.14	5.44±0.83
3	20.17±4.95	8.43±2.25	5.97±2.10
P Value	NS	NS	NS

Table 3. Mean concentrations (µg metal/g d.w.) and associated standard deviations of copper in the gill, liver and muscle of fishes *Mullus barbatus* (MB), *Caranx crysos* (CC) and *Mugil cephalus* (MC). See Table 1 for details.

Station	Gill	Liver	Muscle
MB 1	7.30±3.38	9.45±2.58	5.88±5.92
2	10.25±2.51	9.91±1.62	2.87±0.34
3	7.10±1.23	12.26±1.51	2.26±0.85
P Value	NS	NS	NS
CC 1	9.57±2.62	28.05±15.84	3.40±1.09
2	16.99±4.68	15.93±2.35	6.15±1.50
3	9.14±0.37	9.46±3.44	2.74±0.61
P Value	0.018	0.016	0.009
MC 1	7.10±2.21	302±174	4.41±1.71
2	6.18±1.45	146±85.4	5.12±1.80
3	7.74±0.56	242±160	3.92±1.27
P Value	NS	NS	NS

Table 4. Mean concentrations (µg metal/g d.w.) and associated standard deviations of chromium in the gill, liver *and* muscle of fishes *Mullus barbatus* (MB), *Caranx crysos* (CC) and *Mugil cephalus* (MC). See Table 1 for details.

Station	Gill	Liver	Muscle
MB 1	8.70±4.43	1.34±0.41	1.60±0.87
2	3.63±1.19	1.22±0.31	1.06±0.25
3	4.68±0.66	2.38±0.42	1.91±0.30
P Value	NS	0.04	0.04
CC 1	8.82±8.03	3.11±0.84	1.48±0.41
2	4.51±0.64	2.88±0.73	2.07±0.50
3	5.32±0.88	1.45±1.05	1.10±0.39
P Value	NS	NS	0.026
MC 1	4.83±3.00	2.54±1.88	1.28±0.47
2	3.20±0.34	1.29±0.10	1.24±0.22
3	4.06±0.76	2.26±0.38	1.35±0.40
P Value	NS	NS	NS

Table 5. Mean concentrations (μg metal/g d.w.) and associated standard deviations of nickel in the gill, liver and muscle of fishes *Mullus barbatus* (MB), *Caranx crysos* (CC) and *Mugil cephalus* (MC). See Table 1 for details.

Station	Gill	Liver	Muscle
MB 1	15.83±6.06	5.51±0.96	6.07±4.60
2	13.08±4.30	4.69±1.07	2.88±0.94
3	10.56±0.97	4.86±1.81	3.05±0.60
P Value	NS	NS	NS
CC 1	11.20±2.67	11.23±1.73	4.80±1.06
2	10.39±2.50	3.50±0.67	2.50±0.54
3	11.44±1.86	1.70±0.62	1.89±0.57
P Value	NS	0.002	0.005
MC 1	11.22±2.49	8.55±3.53	4.25±0.86
2	8.10±1.82	4.68±1.21	3.02±0.90
3	8.47±1.61	4.75±0.40	2.25±0.95
P Value	NS	0.017	0.016

Table 6. Mean concentrations (μg metal/g d.w.) and associated standard deviations of zinc in the gill, liver and muscle of fishes *Mullus barbatus* (MB), *Caranx crysos* (CC) and *Mugil cephalus* (MC). See Table 1 for &ails.

Station	Gill	Liver	Muscle
MB 1	30.5±10.8	35.3±8.33	16.1±11.4
2	57.0±13.9	36.2±7.09	19.3±2.37
3	55.7±7.22	55.3±9.84	25.8±19.3
P Value	<0.05	<0.05	NS
CC 1	40.3±9.28	76.2±19.0	31.4±3.42
2	67.7±5.62	67.7±7.93	33.6±3.66
3	51.6±12.4	27.3±14.6	18.0±4.11
P Value	<0.01	<0.001	<0.001
MC 1	35.2±7.35	52.2±16.9	23.5±3.60
2	42.4±9.58	40.8±8.35	24.0±3.87
3	52.0±9.99	57.3±12.3	30.9±9.98
P Value	<0.05	NS	NS

Table 7. Mean concentrations (μg metal/g d.w.) and associated standard deviations of iron in the gill, liver and muscle of fishes *Mullus barbatus* (MB), *Caranx crysos* (CC) and *Mugil cephalus* (MC). See Table 1 for details.

Station	Gill	Liver	Muscle
MB 1	263±32.9	151±45.9	71.7±42.3
2	299±112	135±22.4	32.2±11.1
3	297±41.6	258±31.8	103.1±44.9
P Value	NS	<0.001	<0.05
CC 1	231±55.4	522±149	59.6±15.6
2	173±38.1	262±52.0	36.4±13.6
3	270±50.0	162±99.0	66.8±34.9
P Value	<0.05	<0.001	NS
MC 1	238±57.9	310±148	73.4±35.8
2	189±34.5	197±42.3	61.1±11.8
3	231±35.7	262±66.5	129 ±69.3
P Value	NS	NS	NS

The three fish species with different ecological needs from the north-east Mediterranean Sea showed high metal concentrations in their tissues at all stations. Results generally showed that metal concentrations were always lowest in the muscle and highest in the gill and liver. This is probably due to their physiological roles in fish metabolism. It has been shown that target tissues of heavy metals are metabolically active ones, like the liver, kidney and gill. Therefore, metal accumulation in these tissues occur higher level compared to some other tissues like the muscle, where metabolic activity is relatively low (Heath, 1987; Langston, 1990; Serra et al., 1993; Roesijadi and Robinson, 1994; Canli et al., 1998).

It is generally agreed that heavy metal uptake occurs mainly from water, food and sediment. However, effectiveness of metal uptake from these sources may differ in relation to ecological needs and metabolism of animals and also contamination gradients of water, food and sediment as well as some other factors such as salinity, temperature, interacting agents (Heath, 1987; Langston, 1990; Roesijadi and Robinson, 1994). Kilgour (1991) indicated that animals which have close relationship with sediment, show relatively high body concentrations of cadmium, although uptake from water was more important route than uptake from sediment for animals which do not burrow. Canli and Furness (1995) also showed that tissue distribution of metals in the Norway lobster *Nephrops norvegicus* differed significantly following to an uptake protocol from food and from seawater. Ecological needs of fishes are also one of the most important factors in the accumulation of heavy metal. For example, in the eel *Anguilla anguilla,* whiting *Merlangius merlangius,* flounder *Platichthys flesus* and plaice *Pleuronectes platessa,* levels of Zn, Cu, Pb and Cd in the muscle ranged considerably (Wharfe and Van Der Broek, 1977). They indicated that generally levels in the bottom dwelling eels are higher than in plaice and flounder, which in turn are higher than levels in whiting. However, in the present study ecological needs of the fishes did not play an outstanding role as all the fish species regardless of their ecological needs showed high metal concentrations. This may iudicate the contamination of both different fish feed and water bodies (e.g. surface and bottom).

Data from the literature showed that metal concentrations in the tissues of fish varied widely depending on where the animals were caught. Doganoc (1995) found that fishes from Slovania contained (ppm w.w.) <0.05-0.34 Pb, <0.003-0.05 Cd, in the muscle between the period of 1982-1993. Serra et al. (1993) showed that in tissues of *Liza ramada* and *Leuciscus cephalus* fished from the northern Adriatic, zinc levels were higher in the chubb than the grey mullet. They also found that the concentrations of iron and copper in the red muscle of the grey mullets were remarkably high and they indicated that this was probably due to swimming activity of this species. Remarkably high copper concentrations in the liver of the grey mullets in the present study support the high copper concentrations of this species. Also it is interesting to note that in the present study *Mugil cephalus* was the only fish species that did not show significant variations (except two cases) among stations and this may also be related to its swimming activity. Medina et al. (1986) measured the concentrations of heavy metals in the muscle of *Mullus barbatus* and *Mullus surmelatus,* collected from Spanish coasts. They found that Cd, Pb and Cr levels ranged between 0.019-0.187, 0.03-0.803 and 0.023-0.638 µg/g d.w. These values are lower when compared to the present results. However, studies from western Turkish coasts also showed high levels of metals in fishes (Uysal and Tuncer, 1982), like the present study. Similarly, in the gulf of Izmir (Turkey), Gey (1985) also found high concentrations of Cu, Zn, Pb, Cr and Cd in the tissues of the bass *Dicentrarchus labrax* and sole *Solea vulgaris*. Iron and zinc concentrations also may vary between different fish species as a result of their biological needs. For example, iron and zinc concentrations in the muscle of various marine fishes from Bangladesh ranged between 8.50-22.2 ppm w.w. for iron and 7.40-22.5 ppm w.w. for zinc (Quazi et al. 1995). The present study also showed that iron and zinc concentrations also varied among the fishes.

Concentrations of Cd, Cr, Cu and Zn in the muscle of the Eastern Mediterranean fishes (Israel) ranged between 0.01-0.90, 0.03-5.82, 0.12-14.7 and 6.7-58.8 ppm d.w. respectively, which are similar to the present results (Hornung and Ramelow, 1987). Heavy metal (Ni, Cu, Pb, Cd and Cr) concentrations in the muscle of six marine fishes from Arabian Sea seem to be lower than the present study (Ashraf and Jaffar, 1989). This is perhaps due to the Mediterranean Sea is more polluted than the Arabian Sea as a result of many industrialised countries around it. Windom et al. (1987) found even lower concentrations of Cd, Cu, Pb, Ni in the muscle of fish *Coryphaenoides armatus* sp from the Atlantic and the pacific Oceans. Concentrations of Cd, Cu, Pb, were between 0.025-0.027, 0.034-0.086, 0.012-0.016 and 0.087-0.46 ppm dry weight respectively. These values are very low comparing the data obtained in the present study. Romeo (1987) also found relatively low concentrations of Cu, Zn, Cd and Pb in the muscle of *Mugil cephalus* (mullet roe) from the northern coast of Mauritania in the Atlantic Ocean as 2.3, 142, <0.1, <0.5 ppm d.w. respectively. However, this is not surprising because oceans are less contaminated marine environments comparing to seas that generally face human impact more than oceans.

This study also emphasised that some metal levels were higher than the acceptable values for human consumption set by various health organisations. For example, Cd and Pb data given in the present study are considerably high compared to daily tolerable cadmium and lead intake from food according to WHO/FAO committee’s proposal (Merian, 1991). These are approximately 1 µg Cd/kg body weight and 7 µg Pb/kg body weight.

This study showed that heavy metal concentrations in the tissues of fishes, regardless of their ecological needs, were considerably high at all stations from the northeast Mediterranean Sea compared to metal concentrations in the literature given above from other waters. This may indicate the contamination of these water bodies and different fish feed. These results indicate that some measures should be taken to prevent the contamination of the marine environment for human and animal health and this may be achieved. For example, Clerk et al. (1995) indicated that concentrations of Hg, Cd, Cu, Zn and Pb in sole from Belgian catches of the North Sea between 1973-1991 showed significant decline in heavy metal concentrations in recent years.

Acknowledgment. This study was supported by the research fund of University of Çukurova.

REFERENCES

Ashraf M, Jaffar M (1989). Trace metal content of six Arabian Sea fish species using a directacid based wet oxidation method. Toxicol Environ Chem 19: 63-68.

Ay Ö, Kalay M, Tamer L, Canli M (1999). Copper and lead accumulation in tissues of a freshwater fish Tilapia zillii and its effects on the branchial Na,K-ATPase activity. Bull Environ Contam Toxicol 62: 160-168.

Bryan G, Langston WJ (1992). Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: a review. Environ Pollut 76: 89-131.

Canli M, Furness RW (1993a). Heavy metals in tissues of the Norway lobster *Nephrops norvegicus:* Effects of sex, size and season, Chem Ecol 8: 19-32.

Canli M, Furness RW (1993b). Toxicity of heavy metals dissolved in sea water and influences of sex and size on metal accumulation and tissue distribution in the Norway lobster *Nephrops norvegicus.* Mar Environ Res 36: 217-236.

Canli M, Furness RW (1995). Mercury and cadmium uptake from seawater and from food by the Norway lobster *Nephrops norvegicus.* Environ Toxicol Chem 14: 819-828.

Canli M, Ay Ö, Kalay M (1998). Levels of heavy metals (Cd, Pb, Cu, Cr and Ni) in tissues of *Cyprinus carpio, Barbus capito* and *Chondrostoma regium* from the Seyhan River, Turkey. Turkish J. Zoology 22: 149-157.

Clerck R de, Vyncke W, Guns M, Hoeyweghen P van (1995). Concentrations of mercury, cadmium, copper, zinc and lead in sole from Belgian catches (1973-1991). Mededelingen Faculteit Lanbouwkundige en Toegepaste Biologische Wetenschappen. Universiteit Gent (Belgium) 60: 1-6.

Doganoc DZ (1995). Heavy metals concentrations in freshwater and marine fishes in period 1982-1993. Zbornik Biotehniske Fakultete Univerze v Ljubljani (Slovania). Kmetijstvo (Zootehnika) 66: 89-97.

Gey H (1985). Izmir korfezinden avlanan levrek *(Dicentrarchus labrax* L.) ve dil baliklarinin *(Solea vulgaris* Quensel) doku ve organlarindaki bazi iz elementlerin (Cu, Mn, Fe, Pb, Co, Cr, Cd) birikim duzeyleri. V. Ulusal Spektroskopi Simpozyumu, 23-25 Eylul, Sivas, Turkey 188-199.

Heath AG (1987). Water pollution and fish physiology. CRC press, Florida, 245 pp.

Homung H, Ramelow GJ (1987). Distribution of Cd, Cr, Cu, and Zn in Eastern Mediterrenean fishes. Mar Pollut Bull 18: 45-49.

Kilgour BW (1991). Cadmium uptake from cadmium-spiked sediments by four freshwater invertabrates. Bull Environ Contam Toxicol 47:70-75.

Langston WJ (1990). Toxic effects of metals and the incidence of marine ecosystems. In: Furness RW, Rainbow PS, editors. Heavy Metals in the Marine Environment. CRC Press, New York 256 pp.

Mance G (1987). Pollution threat of heavy metals in aquatic environment. Elsevier, London, 363 pp.

Merian E (1991). Metals and Their Compounds in the Environments. Occurrence, Analysis and Biological Relevance. ISBN 0-89573 - 562 - 8 (VCH New York).

Medina J, Hernandez F, Pastor A, Beferfull JB, Barbera JC (1986). Determination of mercury, cadmium, chromium and lead in marine organisms by flameless atomic absorption spectrophotometry. Mar Pollut Bull 17:41-44.

Quazi S, Banu CP, Rahman MM, Sayeed S (1995). Mineral content of fresh water and marine fish species. Proceedings of the third Asia-Pasific food analysis Network Conference on Food Analysis. P.2, (IRRI call no. TX511 C65).

Roesijadi G, Robinson WE (1994). Metal regulation in aquatic animals:Mechanism of uptake, accumulation and release. In: Malins DC, Ostrander GK, editors. Aquatic Toxicology (Molecular, Biochemical and Cellular Perspectives), Lewis Publishers, London, 539 pp.

Romeo M (1987). Trace metals in fish roe from the Mauritania coast. Mar Pollut Bull 18:507-508.

Serra R, Carpene E, Torresani G, Andreucci A, Grandini S (1993). Concentrations of Zn, Cu, Fe, and Cd in *Liza ramada* and *Leuciscus cephalus.* Archivio Veterinario Italiano 44:166-174.

Uysal H, Tuncer S (1982). Levels of heavy metals in some commercial food species in the Bay of Izmir. VI Journees Etud Pollutions Cannes, CIESM, 323.

Windom H, Stein D, Sheldon R, Smith R Jr (1987). Comparison of trace metal concentrations in muscle tissue of a benthopelagic fish *(Coryphaenoides armatus)* from the Atlantic and Pacific oceans. Deep-Sea Research 34: 213-220.

Wharfe JR, Van don Broek WLF (1977). Heavy metals in macroinvertabrates and fish from the lower Medway Estuary, Kent. Mar Pollut Bull 8: 3l-35.