

487

TRACE METAL LEVELS IN FISH AND CRUSTACEA FROM NORTHEASTERN MEDITERRANEAN COASTAL WATERS

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(Received: 15 May, 1981)

ABSTRACT

Some fish and crustacea caught near the northeastern Mediterranean coast of Turkey between 1977 and 1980 have been analysed by the AAS technique for their Hg, Cd, Pb, Zn, Cu, Fe, Ni, Cr and Mn contents. In the crustacea Portunus pelagicus (crab) and Penaeus keratherus (shrimp), the two essential elements Zn and Cu, showed a linear correlation. Among the bony fish, Upeneus moluccensis (gold band goat fish), a member of the Mullidae family, and Portunus pelagicus showed a much greater tendency to accumulate Hg than other species. Although Cr concentrations in the sediments of the area studied were high, Cr levels in the organisms studied were found to be relatively low. The highly toxic metals Hg, Cd and Pb were found to be present in concentrations lower than those reported from other areas of the Mediterranean.

INTRODUCTION

Of all the research on the concentrations of heavy metals in the Mediterranean environment only a little has been carried out in that part of the northeastern Mediterranean known as the Cilician Basin or the North Levantine Sea (Fig. 1) (Ramelow *et al.*, 1978; Balkas *et al.*, 1979; Tuncel *et al.*, 1980; Salihoglu *et al.* (in press); Tugrul *et al.* (1980)). The area is bounded by the Toros Mountains to the north and the Cyprus (Kyrenia) Mountains to the south. The Mersin area (27°08' E, 38°26' N) can be considered as a pollution hot spot, since considerable industrial complexes, e.g. petrochemical, agrichemical, and a busy harbour are located in the area. Inland, agriculture is developed and significant quantities of insecticides, pesticides and fungicides are applied. Of the fungicides, Cu, Zn and Hg compounds are most commonly used (GTHB, 1979).

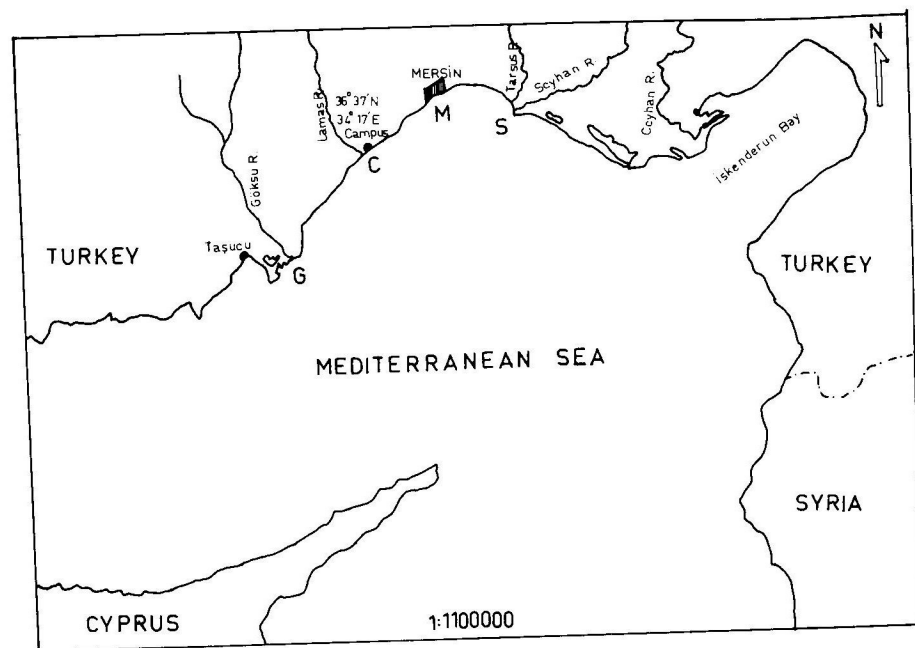


Fig. 1. Study areas.

This paper reports on the concentrations of Hg, Cd, Pb, Zn, Cu, Fe, Ni, Cr and Mn found in bony fish such as *Mugil auratus* and *Mugil saliens* (two different species of grey mullet) and *Mullus barbatus* (striped mullet), *Mullus surmuletus* (red mullet), *Upeneus moluccensis* (goldband goatfish) (these last three are members of Mullidae species), *Boops salpa* (salema), *Sardinella maderensis* (shortbody sardine) and *Pomatomus saltator* (blue fish) and the Crustacea, *Portunus pelagicus* (crab) and *Penaeus kerathurus* (shrimp), caught between 1977 and 1980. The Mullidae were recommended by FAO/UNEP (1975) as monitoring species. The other species were studied since they have high commercial value in the area.

MATERIALS AND METHODS

Samples collected by gill nets and by deep trawling were identified, placed in plastic bags and stored at below -20°C until analysis in accordance with FAO identification and sampling procedures (FAO, 1973; Bernhard, 1976).

Approximately 1 g of fish muscle or the soft part of a crustacean ('abdominal white muscle') was digested with 3 ml concentrated HNO_3 in high pressure decomposition vessels and subsequently diluted to the desired volume with distilled-deionised water.

All the analyses were performed by Varian-Techtron models 1250 and AA-6 atomic absorption spectrophotometers. Mercury analysis was performed by the cold-vapour technique. Other metals were analysed by flame or carbon-rod techniques and background corrections were used as required.

The sediment sampling and analysis procedures given in detail by Ozkan *et al.* (1979) and Tuncel *et al.* (1980) were followed. For mercury determination in sediments and to avoid loss of mercury the wet samples were digested for 9 h at 140°C in high pressure vessels containing conc. HNO_3 ; the sediment was then dried and further digested in an $\text{HNO}_3/\text{HClO}_4/\text{HF}$ mixture for subsequent determination of other heavy metals.

The validity of the results presented in this study is justified by the results obtained on the intercalibration sample (MA-A-2) supplied by International Laboratory of Marine Radioactivity (IAEA), Monaco. As can be seen from Table 1, the results of our laboratory are comparable with the Chauvenet's test results (IAEA, 1980).

TABLE 1
TRACE METALS IN FISH HOMOGENATE (MA-A-2) INTERCALIBRATION EXERCISE CO-ORDINATED BY IAEA MONACO LABORATORIES ($\mu\text{g/g}$, dry weight)

Element	This study	Chauvenet's test results ^a
Hg	0.49	0.47 ± 0.02
Zn	32	33 ± 1
Cu	6.5	4.0 ± 0.1
Fe	50	54 ± 1
Cr	1.7	1.3 ± 0.1
Ni	1.0	1.1 ± 0.2
Mn	1.24	0.81 ± 0.04
Pb	0.45	0.58 ± 0.07
Cd	0.05	0.066 ± 0.004

^a The standard deviations given at 1σ for mean standard error.

RESULTS AND DISCUSSION

The minimum, maximum and average fork lengths and total weights, together with number of specimens and fresh weight to dry weight ratios of the species sampled between 1977 and 1980 are given in Table 2, and the analytical results in Table 3.

The Hg levels in the marine organisms analysed, except *Upeneus moluccensis* and *Portunus pelagicus*, were low and no significant local differences were found. *U. moluccensis* and *P. pelagicus* showed significant ability to concentrate Hg in their tissues and soft parts (0.25 ppm, fresh weight and 0.127 ppm, fresh weight, respectively) as compared with other organisms analysed from the same sites. In

TABLE 2
BIOLOGICAL CHARACTERISTICS OF THE SPECIES ANALYSED

Species	Fork length (mm)			Total weight (g)			FW:DW ^a
	Min.	Max.	Mean	Min.	Max.	Mean	
<i>Penaeus kerathurus</i> ^b	95	215	150	6	86	27	4.0 (31)
<i>Portunus pelagicus</i>	—	—	—	454	1300	875	4.2 (21)
<i>Pomatomus saltator</i>	—	—	—	—	—	—	4.1 (3)
<i>Mugil saliens</i>	195	370	290	83	706	375	4.4 (3)
<i>Mugil auratus</i>	149	360	295	36	696	330	4.6 (46)
<i>Boops salpa</i>	183	204	188	100	164	122	4.7 (9)
<i>Sardinella maderensis</i>	155	230	174	30	180	70	3.9 (7)
<i>Upeneus moluccensis</i>	80	164	129	9	68	34	4.4 (23)
<i>Mullus barbatus</i>	109	188	152	20	107	57	4.2 (19)
<i>Mullus surmuletus</i>	90	255	145	8.2	276	59	4.5 (50)

^a The values given are averages and the numbers in parentheses are the number of specimens used for the determination of average FW:DW (fresh weight to dry weight) ratio.

^b Total length.

addition, a net increase in Hg concentration with size (and thus age) of the fish was observed in *U. moluccensis* sampled from two different locations, Campus (C) and Göksu (G), (Fig. 1). The average Hg values of the same size groups of fishes (145–165 mm fork length) sampled in May 1980 were significantly higher (0.5–0.85 ppm, fresh weight) than *U. moluccensis* sampled in February 1980 (0.33–0.43 ppm, fresh weight).

It is interesting that *U. moluccensis* had an accumulating capacity 4–5 times higher than that of the other Mullidae species (*Mullus barbatus* and *M. surmuletus*) although these are all omnivorous fishes, inhabiting similar areas and ingesting the same small bottom marine organisms. Yannai & Sachs (1978) obtained similar results. *U. moluccensis* might therefore be used as a good indicator of Hg changes in the marine environment.

Some seasonal changes in mercury have been observed in *Mugil auratus*, *Mullus surmuletus* and *Portunus pelagicus*, strongly correlated with the period of Hg fungicide application, with meteorological parameters such as rainfall, and with the physiological changes of the organisms. It has been shown that *M. surmuletus* may be used as an indicator of mercury in coastal seawaters greatly affected by mercury from natural and man-made sources (Tugrul *et al.*, 1980).

Mercury levels in various organisms from the Mediterranean have been compiled by Bernhard (1978). In general, the mercury values we have obtained (Table 3) are lower than those reported from other areas of the Mediterranean (Bernhard, 1978; Yannai & Sachs, 1978; Uysal, 1979; Majori *et al.*, 1979). However, the Hg content of *Mugil auratus* was in the range of values found near Israeli coasts (Levitan *et al.*, 1974), and the results were similar to those found in Atlantic (Bernhard & Zattera, 1975; Stenner & Nickless, 1975) and Australian (Bebbington *et al.*, 1977) waters.

The zinc and copper contents of the crustaceans *Portunus pelagicus* and *Penaeus*

TABLE 3
TRACE METAL CONCENTRATIONS IN CRUSTACEA AND FISH (WET WEIGHT BASIS)

Species	Hg (ng/g)	Zn (µg/g)	Cu (µg/g)	Fe (µg/g)	Ni (µg/g)	Cr (µg/g)	Mn (µg/g)	Pb (µg/g)	Cd (µg/g)
<i>Penaeus kerathurus</i>	8–133 38 ^a (31) ^b	9.3–18.8 13.2 (30)	1.8–12.8 7.4 (27)	<1.5–10.4 3.1 (16)	0.9–2.9 1.4 (3)	0.07–0.33 0.14 (4)	<0.2–0.35 <0.2 (11)	0.34 (1)	0.01–0.07 0.03 (6)
<i>Portunus pelagicus</i>	32–296 132 (21)	19.5–47.9 31.8 (21)	1.7–21.7 9.7 (21)	1.4–6.3 3.5 (19)	0.12 (1)	0.36 (1)	0.29 (1)	0.27 (1)	0.03 (1)
<i>Mugil saliens</i>	—	2.5–3.1 2.8 (3)	0.15–0.73 0.48 (3)	2.9–9.9 6.9 (3)	0.19–0.33 0.26 (3)	9.25–0.44 0.35 (3)	0.37–0.78 0.50 (3)	<0.1–0.53 (3)	<0.01–0.04 (3)
<i>Mugil auratus</i>	1–120 25 (46)	2.7–9.6 4.2 (46)	0.29–1.85 0.52 (31)	0.4–8.2 4.0 (40)	<0.06–0.54 0.24 (7)	0.01–0.85 0.12 (15)	0.16–0.84 0.45 (8)	<0.1–0.79 (7)	<0.01–0.08 (8)
<i>Boops salpa</i>	3–17 8 (3)	4.6–8.2 6.6 (9)	0.27–0.35 (2)	2.9 (1)	—	—	—	—	—
<i>Sardinella maderensis</i>	22–49 (2)	4.4–14.4 9.3 (5)	0.35–1.7 0.72 (4)	—	—	—	<0.22 (4)	—	0.01 (1)
<i>Upeneus moluccensis</i>	43–850 250 (18)	1.6–3.0 2.4 (23)	<0.5–0.72 <0.5 (15)	2.0–4.8 3.5 (11)	—	—	<0.2 (4)	<0.1 (14)	<0.01–0.04 <0.01 (15)
<i>Mullus barbatus</i>	28–88 45 (16)	3.6–7.4 5.1 (19)	0.20–0.69 0.47 (8)	0.7–4.7 2.4 (7)	—	0.14 (1)	<0.2 (7)	<0.1 (5)	0.02–0.04 0.03 (7)
<i>Mullus surmuletus</i>	4–260 67 (42)	2.6–7.2 4.0 (50)	<0.5–0.72 <0.5 (20)	1.0–10.9 3.9 (34)	0.7–1.8 1.1 (4)	0.04–0.17 0.07 (5)	<0.2–0.3 (4)	<0.2 (3)	<0.01–0.13 (10)
<i>Pomatomus saltator</i>	—	5.6–19.5 10.4 (3)	0.51–0.91 0.76 (3)	—	—	—	—	0.42–0.75 (2)	0.03–0.09 (2)

^a The second line refers to the mean values for each metal.

^b The numbers in parentheses give the number of specimens analysed.

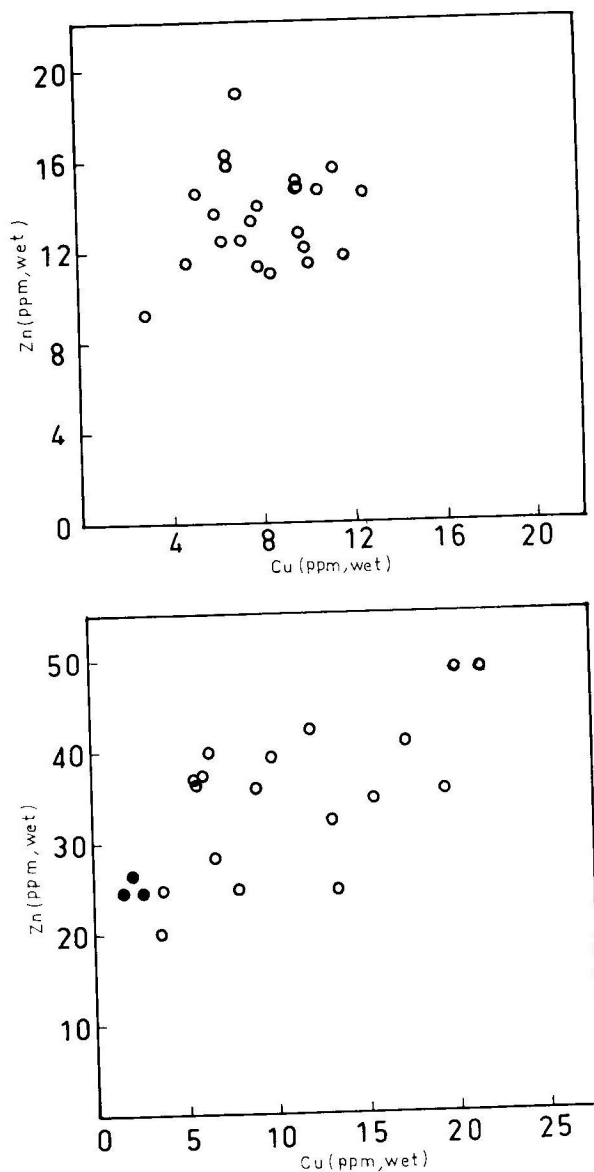


Fig. 2. Zinc concentrations as a function of copper found in (top) *Penaeus kerathurus* and (bottom) *Portunus pelagicus*. For linearity calculations the three blocked circles (●) were rejected according to Chauvenet's test.

kerathurus were higher than the values found in fish, whereas the Cr, Ni, Cd, Pb and Mn contents of both crustacea and fish were of the same order of magnitude. Thus, Cu and Zn concentrations in the tissue of crustaceans were relatively high. Concentrations of both Zn and Cu increased with the increasing total fresh weight of the crustaceans. It will be seen that there was a correlation between Zn and Cu concentrations (Fig. 2). Although there is a scattering in the Zn compared with the Cu plot (Fig. 2), the correlation coefficients are 0.65 and 0.21 for *P. pelagicus* and *P. kerathurus*, respectively. Considering all individuals analysed, the Zn:Cu ratios are 1.8 ± 0.6 for *P. pelagicus* and 3.8 ± 1.8 for *P. kerathurus*. This suggests that both Zn and Cu, which are essential metals for the organisms, are needed for certain physiological processes. In other words, in order to maintain the Zn:Cu ratio, either copper must be absorbed by an active transport process while zinc is being accumulated by the organisms, or excess copper or zinc must be excreted from the body by some other process (Bryan, 1971). That is, these animals are able to regulate the concentrations of Zn and Cu in the body in order to keep the ratio constant, despite changes in the availability of these metals in the environment (Bryan, 1971).

Trace metal levels were generally very low. This was surprising since the concentrations of such metals as Cr, Ni and Mn found in the sediments from the sampling sites were significantly high (Table 4). This indicates that omnivorous (Mullidae) and herbivorous fish and crustaceans do not accumulate these metals and can regulate the concentrations of these elements in their tissues and soft parts. This observation is consistent with the work of Phelps *et al.* (1975), who reported decreasing Cr concentrations within the food web, highest in the sediments and lowest in the bottom feeding organisms.

The two carnivorous fish, *Pomatomus saltator* and *Sardinella maderensis*, appear to have higher concentrations of Zn and Cu than omnivorous and herbivorous fish.

The trace metal contents of *Mugil auratus* from location C (Fig. 1) have been

TABLE 4
TRACE METAL CONCENTRATIONS IN COASTAL WATER SEDIMENTS FROM THE EASTERN MEDITERRANEAN (ppm, dry weight)^{a,b}

Element	Mersin	Campus ^c	Seyhan Delta
Zn	66–70	47–74	55–70
Cu	27–29	23–27	20–32
Hg	0.44–0.48 ^d	0.022–0.034 ^d	—
Ni	285–290	330–560	240–250
Cr	175–180	530–590	150–160
Fe	45–50	40–45	42–60
Mn	390–610	715–790	—

^a Hg concentration ppm, wet weight, Fe: g/kg dry weight.

^b Hg in sea water (at Campus location): 0.00001 ppm, whereas 30–70% of Hg is associated with suspended particulate matter (Tuncel, 1978).

^c Ozkan *et al.* (1979).

^d Tuncel *et al.* (1980).

discussed by Salihoglu *et al.* (1980). The present work extends the analytical results to include species from other regions and shows how Zn concentrations in *Mugil auratus* sampled between 1978 and 1980 vary with the size of fish and the season.

Fe and Hg concentrations in shrimp and crab were lower than those obtained by Fukai & Broquet (1965) and Bertine & Goldberg (1972), but Cr and Zn concentrations were within the range of these investigators' results. Fish tissues from Israeli coastal waters contained higher Zn, Cu, Cr, Pb and Cd values (Roth & Hornung, 1977). However, Cr, Cu and Zn concentrations in sediments from Israeli coasts (Roth & Hornung, 1977) were much lower than our sediment concentrations. Our average results for Cd, Cu and Zn in *Mullus barbatus* (Table 3) are similar to tentative 'typical' metal concentrations in *Mullus barbatus* given by Bernhard (1978).

The Fe to Cr ratios in all investigated samples varied from 17 to 34. Fukai & Broquet (1965) claimed that the Fe:Cr ratio might have a value of 0.3×10^3 , but our results contradict this.

CONCLUSIONS

- (1) The data given in Table 2 may be useful as a tentative 'baseline' against which future changes within the study area can be correlated.
- (2) *Upeneus moluccensis* should be selected as a monitoring organism for Hg accumulation in the edible part of the fish.
- (3) There is a relationship between Zn and Cu contents in the crustaceans, *Portunus pelagicus* and *Penaeus kerathurus*.
- (4) The trace metal levels of commercially important marine organisms are below the tolerance levels set by the National Health and Medical Research Council (Bebbington *et al.*, 1977), with the exception of Hg in larger specimens of *Upeneus moluccensis*.

ACKNOWLEDGEMENTS

We are very grateful to NATO (NATO Research Grant No. 1943) for partial financial support, and to Dr A. F. Gaines and Miss T. Aydogdu for their valuable comments and suggestions.

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