Bull. Environ. Contam. Toxicol. (1996) 56:766-773

Bulletin of Environmental Contamination and Toxicology

Heavy Metals in Different Fishes from the Middle Eastern Coast of Tunisia

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Received: 3 August 1995/Accepted: 15 November 1995

Considerable information has been reported on trace metal concentrations of various fishes in the Mediterranean area (Roth and Hornung 1977; Leonzio et al. 1981; Capelli et al. 1983; Demirkurt et al. 1990), but there is a lack of data on the concentrations of trace metals in fishes from the southern Mediterranean. For this reason, work was done to establish a baseline of heavy metal concentrations in fishes from the coast of Sfax (middle eastern coast of Tunisia). This coast has been industrialized for many years. Nevertheless, touristic activities have been developing for the last several years.

The objectives of the present work were to establish an accumulation pattern of copper, cadmium and zinc in individual organs (muscle, liver and gonad) of fishes.

MATERIALS AND METHODS

Fishes were collected during September and October 1989, at various stations along the middle eastern coast of Sfax (Tunisia, Fig. 1). Fishes were identified, weighed and different tissues were dissected out. Samples of muscle, gonad, and liver from each specimen were stored at -80°C until analysis. For analysis, samples were thawed and dried to constant weight, then digested (0.3 - 1.4 g) in teflon beakers with suprapur nitric acid (65%) on a hot plate for 4 hr. The resulting solution was evaporated to dryness and redissolved in 0.1N nitric acid to a final volume of 20 mL. Appropriate blanks and standard reference material were prepared for analysis at the same time. Analyses were carried out by atomic absorption spectrophotometry (Philips, Pye Unicam SP9). A graphite furnace with background correction was used in the case of cadmium. Copper and zinc were analyzed by an air-acetylene flame.

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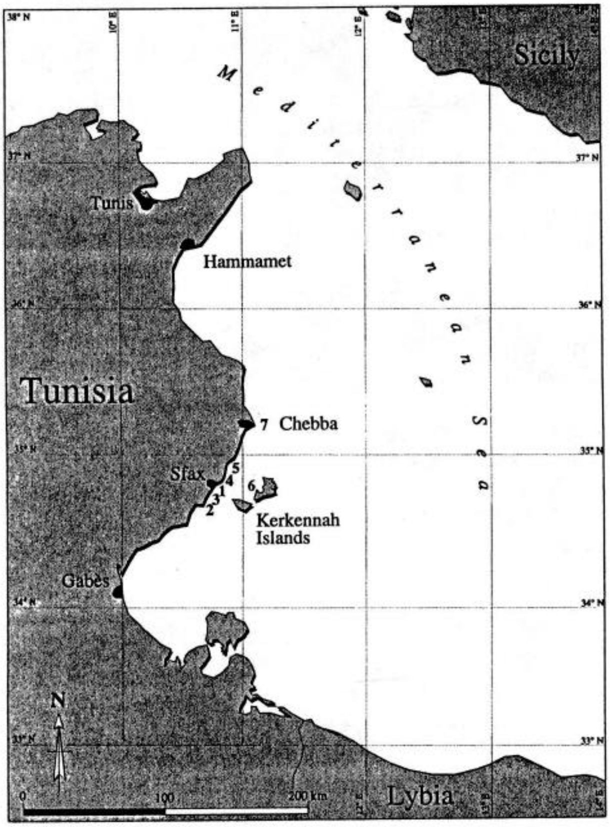

Figure 1. Sampling locations for fish collections in the southern Mediterranean Sea (Tunisian Coast)

The analytical procedure was calibrated against a standard reference material, lobster hepato-pancreas (TORT-l provided by the National Research Council of Canada). Results of these analyses are given in Table 1. Our results are in agreement with the certified values.

Table 1. Comparison of metal concentrations (μg/g dry weight) in standard reference material (lobster hepato-pancreas), certified by the National Research Council of Canada (NRCC), and our values (n=5).

Metal	NRCC values	Our values
Cd	26.3 ± 2.1	24.1 ± 0.6
Cu	439 ± 22	420 ± 20
Zn	177 ± 10	165 ± 10

RESULTS AND DISCUSSION

Stations 1 to 5 have coastal characteristics and are influenced by industrial activities, urban wastes and the harbour of Sfax. Station 6 is located 20 km from the coast, near the tourist islands of Kerkennah, far from industrial effluents. Station 7 at Chebba, i.e., 60 km North from Sfax, is not affected by any known pollution source and has been considered as a control area in this work (Fig. 1).

To assess the possible impact of pollution in metal concentrations found in fish, twenty-two samples of the annular seabream *Diplodus annularis* (Sparidae) were collected at Stations 1 to 6 (group 1) and compared to thirteen samples of the same fish taken at station 7 (group 2). Results are shown in Table 2.

Table 2. Heavy metal concentrations (µg/g dry weight) in organs of *Diplodus annularis* collected in the Gulf of Gab&s (group 1) or at 60 km to the North (Chebba, Station 7, group 2). Mean values ± 1 standard deviation

Stations 1 to 6 Group 1; n=22	Cd	Cu	Zn
muscle	0.10 ± 0.07	2.10 ± 0.27	34 ± 2
liver	2.26 ± 0.91	29.3 ± 8.6	125 ± 8
gonad	1.04 ± 0.32	12.1 ± 2.6	690 ± 39
Station 7 Group 2; n=13			
muscle	<0.03*	0.59 ± 0.07*	20 ± 1*
liver	<0.03*	19.3 ± 4.0	122 ± 9
gonad	<0.03*	2.43 ± 0.30*	509 ± 17*

*t-tests significant between the means of group 1 and group 2 at $p<0.05$

Organs from *Diplodus annularis* sampled at Station 7 generally showed lower concentrations (particularly Cd and Cu) than those from the other stations (t-tests between group 1 and group 2 showed significance at $p<0.05$ for Cd in the muscle, liver and gonad, for Cu in muscle and gonad and for Zn in muscle and gonad). Station 7 can be considered as clean compared to the other stations. At station 6, previously considered as a control area, *D. annularis* had Cd concentrations of 0.18

μg/g in the muscle, 5.83 μg/g in the liver and 0.35 μg/g in the gonads which are higher than the mean Cd values for group 1 (Table 2). The circulation of waters in the Gulf of Gabès may carry pollution from the continental coast towards the islands, surrounded by shallow waters.

Table 3 shows heavy metal concentrations in the different organs of four fishes collected from Stations 1 to 6: the bogue, *Boops salpa* (Sparidae); the golden grey mullet, *Liza aurata* (Mugilidae); the brown meagre, *Corvina nigra* (Sciaenidae); the common sole, *Solea vulgaris* (Soleidae) .

Table 3. Mean Cd, Cu and Zn concentrations (μg/g dry wt)in the organs of the fishes collected from Stations 1 to 6. Standard deviations (s.d.) are also shown

Organ /Species	N	Cd	Cu	Zn
Muscle				
B.salpa	4	0.05	3.15	53
s.d.		0.01	0.70	3
L.aurata	8	0.09	5.70	32
s.d.		0.06	0.40	5
C.nigra	4	0.15	5.65	33
s.d.		0.03	0.30	1
S.vulgaris	7	0.05	2.98	29
s.d.		0.01	0.40	2
Liver				
B.salpa	4	4.88	26.5	104
s.d.		0.90	2.3	5
L.aurata	8	6.23	276	160
s.d.		1.56	57	6
C.nigra	4	1.34	11.5	43
s.d.		0.20	1.1	3
S.vulgaris	7	2.51	278	108
s.d.		0.43	50	36
Gonad				
B.salpa	4	0.09	5.10	870
s.d.		0.01	1.10	139
L.aurata	8	0.22	3.00	515
s.d.		0.01	0.40	122
C.nigra	4	0.25	6.14	1048
s.d.		0.05	0.10	49
S.vulgaris	7	0.42	6.10	813
s.d.		0.03	0.10	54

The mean values reported in Table 3 are compared to metal concentrations in *Diplodus annularis* collected at stations 1 to 6 (Table 2). In all the fish species, Cd concentrations in the muscle were low (generally<0.2 µg/g) and did not vary much according to the species. Compared to muscle, the liver presented higher Cd concentrations, especially in *Boops salpa* (4.88 µg/g) and in *Liza aurata* (6.23 µg/g). The highest Cd value determined in gonads was noted for *D. annularis.* Copper concentrations were low in the muscle (from 1.5 to 7.0 µg/g, Tables 2, 3). *Liza aurata* and *Solea vulgaris* accumulated Cu, particularly in the liver (276 and 278 µg/g, respectively). These values are 10 to 20 times higher than those found for *B. salpa, D. annularis* and *Corvina nigra.* The highest Cu value analyzed in the gonad was found for *D. annularis.* Zinc concentrations in the muscle ranged from 25 to 60 µg/g and from 34 to 150 ug/g in the liver. All fish species were characterized by high mean zinc concentrations in the gonad, from 515 µg/g (*L. aurata*) to 1048 µg/g (*C. nigra*).

The fish liver concentrated Cd and Cu more than muscle or gonad, whereas the gonad had higher Zn values compared to muscle or liver. Differences found in the concentrations of Cd and Cu in the liver of the fishes analyzed may be attributed, in part, to their food habits. *Diplodus annularis* is herbivorous, whereas the other fishes are omnivorous. *Liza aurata* is a particularly voracious species and is often encountered in waste water outlets. *Solea vulgaris* is a benthic species feeding on organisms living in the sediments. Increased metal concentrations in liver may represent storage of metals. Metal detoxication occurs mainly in the livers of fish which may also present high levels of metallothioneins (MT) when exposed to metal contamination (Duquesne and Richard 1994). This has been also demonstrated for the benthic fish *Scorpaena porcus* (Scorpaenidae), collected from the coast of Sfax (Hamza-Chaffai 1993). Nevertheless, correlations between total heavy metal concentration in the liver and MT content are not always significant (Overnell and Abdullah 1988). The MT content is more likely correlated to the cytosolic fraction content of metal (Hamza-Chaffai 1993; Roesijadi 1994; Romeo and Gnassia-Barelli in press). Cosson et al. (1991) hypothesized that MT levels cannot be used directly as biological indicators of pollution. The results reported here demonstrated that Cd and Cu concentrations in the livers may be good biomonitors for the four fishes studied (Table 3).

High zinc values in gonads may be explained by the fact that this essential metal plays a physiological role in fertilization; it is stored as a reserve in female oocytes. Julshamn and Braekkan (1976) reported that the zinc level in the ovary of *Gadus morhua* (Gadidae) was higher than in any other organ of the fish. Zinc was found to be more concentrated (ca 10 times) in the gonad of *Mugil cephalus* (Mugilidae) than in the muscle (Romeo 1987), which is in agreement with what we found for the Mugilidae *Liza aurata* (ratio: Zn in gonad to Zn in muscle=16).

The results reported here were compared to the data published in the literature on metal concentrations in muscle from different fishes (Table 4). Two other species belonging to the Mugilidae: the flathead grey mullet, *Mugil cephalus* (n=4) and the thicklip grey mullet, *Mugil* (*Chelon*) *labrosus* (n=4), collected at Stations 3, 4 and 5, were analyzed for their metal content in muscle (results given in Table 4).

Table 4. Heavy metal concentrations in edible muscle of different fishes from various areas of the Mediterranean. Concentrations are expressed as μg/g dry wt (* wet wt). Mean values or ranges () are shown

Species	Cd	Cu	Zn	References
Sparidae				
D.annularis	0.10	2.10	34	This work
D. vulgaris	0.30	4.2	26.5	Roth and Hornung (1977)
D. sargus	0.03			Pastor et al. (1994)
B. boops	0.05	3.15	53	This work
B. boops	(0.03 0.06)	(0.30 2.81)	(17.6 28.2)	Hornung and Ramelow (1987)
Pagellus erythrinus	0.02	6.90	16.50	El Nabawi et al. (1987)
Mugilidae				
L. aurata	0.09	5.7	32	This work
L. aurata	0.05*	0.7*	10.6*	UNEP (1989)
M. cephalus	0.07	4.78	45	This work
M. labrosus	0.02	2.96	33	This work
Soleidae				
S. vulgaris	0.05	2.98	29	This work
S. vulgaris	0.54	2.90	20	Demirkurt et al. (1990)
S. solea	0.20	1.40	22	Roth and Hornung (1977)

The concentrations of metals for edible muscle of fish, reported in Table 4, are below those likely to cause a public health problem: 2 µg Cd/g (dry weight), according to the U. S. Food and Drug Administration (*in* Arnac and Lassus 1985) or 150 µg Cu/g and 5 mg Zn/g according the National Health Medical Research Council of Australia (*in* Bebbington et al. 1977). All the values reported by the different authors are in good agreement with our values.

In conclusion, this study fills a gap by providing information on heavy metal concentrations in different fish species from the mid-eastern coast of Tunisia, an area of increasing tourism. This work demonstrates that heavy metal concentrations in the muscle and the gonad of the commercially important fish *Diplodus annularis* are higher when fish were collected near the coast of the area of Sfax, which is highly industrialized, or in the waters influenced by this area than further to the North (Table 2). In the area of Sfax, different fish species were shown to present high cadmium and copper concentrations in the liver (Table 3). Metal concentrations in fish liver may represent good biomonitors of metal pollution. Some fish species even exceeded the tolerable limits of cadmium and copper in their livers. However, fish livers are very seldom consumed except in restricted areas where the daily intake is fortunately low. Gonads of all fish species showed high levels of zinc, which are, nevertheless, much below the limits.

Acknowledgments. The authors thank S. Maklouf and S. Drira for their efforts in sample collection and Dr. M. Gnassia-Barelli and T. Juhel for help in heavy metal determinations, carried out in France. Work was supported by a French-Tunisian cooperation agreement.

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