

Distribution and Concentration of Trace Metals in Tissues of Different Fish Species from the Atlantic Coast of Western Africa

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Growing interest has been shown in the fate of metals in estuarine and coastal environments and open ocean ecosystems from all climatological regions in the world (Everaats and Nieuwenhuize 1995). Metals are toxic to most marine organisms as they are to man. They can reach us through seafood. It is, therefore, important to determine the concentration of metals in edible marine organisms. In this respect, few data concern the metal levels in organisms from the African coasts. For a long time, Africa was thought to be safe from aquatic pollution (Biney et al. 1994). Recently, there has been considerable interest in establishing the degree of contamination of African aquatic ecosystems by heavy metals. The need to make an assessment of the contamination in the African environment has led to the initiation of several pollution monitoring programmes and research work at various scientific institutions in the region (Biney et al. 1994). Mauritania coastal waters are among the most productive in the world, supporting abundant fish populations which are harvested as food. Potential contamination of fish with metals might be crucial for the exploitation of this resource. In a previous paper (Roméo et al. 1999), data on metals in some fish species collected off Nouakchott were presented. In the present paper, more fish species were analyzed to have a full insight on metal concentrations of pelagic, benthopelagic and demersal fish.

MATERIALS AND METHODS

Fish from different species were collected by professional fishermen in January 2003, using their traditional methods with pirogues equipped with outboards motors. When boats reach the fishing zone off the town of Nouakchott (18°N, 16°W), motors are switched off and fishermen are angling with lines. Immediately after collection, fish samples were brought to the laboratory. Samples were dissected to separate muscles, gills, livers. Sex was determined and gonads collected when possible. The samples were dried to constant weight 50°C, wrapped in parafilm. Dried samples (ratio wet wt./dry wt. = ca 5) were taken to the Laboratory of Nice, France. Samples were prepared under a laminar flow hood and digested (duplicate digestion in each case) with Suprapur nitric acid 65% Merck in a microwave oven. Cd, Cu and Zn analyses were carried out directly on the digested solution, using an atomic absorption spectrophotometer equipped with an air-acetylene flame or with a graphite furnace.

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Table 1. Analysis of the reference material lobster hepatopancreas Tort-2 (National Research Council Canada). Mean values \pm 1 standard deviation.

| Metal | Certified values ($\mu\text{g g}^{-1}$ dry wt) | <i>n</i> | Recorded values |
|-------|---|----------|-----------------|
| Cd | 26.7 \pm 0.6 | 5 | 27.0 \pm 0.7 |
| Cu | 106 \pm 10 | 5 | 101 \pm 1 |
| Zn | 180 \pm 6 | 5 | 177 \pm 2 |

Deuterium background correction was used when necessary. The analytical procedure was checked using a standard reference material. The results shown in Table 1. The results demonstrate that that metal analyses are in good agreement with the certified values. Moreover, metals are not lost during the digestion procedure. The limits of detection for flame analysis are 0.012 mg Cd l⁻¹, 0.015 mg Cu l⁻¹, 0.005 mg Zn l⁻¹; for furnace analysis 0.3 $\mu\text{g Cd l}^{-1}$ and 3 $\mu\text{g Cu l}^{-1}$, zinc was always determined with the flame.

RESULTS AND DISCUSSION

Table 2 describes the class, species, the living zone and the feeding habits of fish. One species of cartilaginous fish, *Rhinobatos cemiculus* (Rhinobatidae, guitarfish), was also collected, it is a demersal species eating on invertebrates. Among bony fish, the caught species were either pelagic : *Dicentrarchus punctatus*, benthopelagic (5 species) or demersal (5 species). Moreover, one Serranidae *Epinephelus marginatus* is reef-associated. Table 2 shows the great diversity of food consumed by the different species. Among the fish eating on molluscs, some such as *D. punctatus*, *E. marginatus*, *Mycteroperca rubra*, consume cephalopods whereas others (*Pseudupeneus prayensis*, *Pegusa lascaris*, *Pagrus caeruleostictus*) eat on bivalves. Species can use as prey both cephalopods and bivalves, i.e. molluscs, this is the case of *Parapristipoma humilae*, *Pagrus auriga* and *Diplodus bellottii*. Metal concentration in the muscle was considered since this tissue is consumed locally or exported. Gills and livers were also chosen as target organs for assessing metal accumulation. Gonads from males or females were analyzed when possible. Table 3 gives the concentrations of metals in the muscles and gills of 9 species. When all tissues could be analysed in several specimens of the same fish species, the results are presented in Fig. 1 ; this was the case for the cartilaginous fish *Rhinobatos cemiculus* (n = 3) and the bony fish *D. punctatus* (n = 7), *Cephalopholis taeniops* (n = 10), *Diplodus bellottii* (n = 2), *P. caeruleostictus* (n = 7). Mean cadmium concentrations in the muscle (Table 3 and Fig. 1) are ranging from 0.005 $\mu\text{g g}^{-1}$ in *Argyrosomus regius* and the highest in *Pegusa lascaris* (0.273 $\mu\text{g g}^{-1}$), whereas the other species have a mean cadmium concentration ranging from 0.040 for *Pagrus auriga* to 0.168 $\mu\text{g g}^{-1}$ for *Epinephelus marginatus*. Gills generally present higher Cd concentrations than muscles, values such as 0.272 $\mu\text{g g}^{-1}$ are found for *Pseudupeneus prayensis*, and 0.313 $\mu\text{g g}^{-1}$ for *P. auriga*. The liver (Fig. 1) particularly concentrates cadmium with mean values ranging from 0.988 (*Rhinobatos cemiculus*) to 17.94 $\mu\text{g g}^{-1}$ (*Diplodus bellottii*). As regards gonad concentrations (Fig. 1), they are not elevated in the cartilaginous fish *R. cemiculus* (ca 0.05 $\mu\text{g g}^{-1}$ males and females) and in the pelagic *Dicentrarchus punctatus* (ca 0.08 $\mu\text{g g}^{-1}$ males and females).

Table 2. Bony fish species, their habitat and their feeding habit along the Mauritania coast.

| Class | Species | Environment | Feeding habit in the West Africa coast |
|------------|--|---------------------|---|
| Haemulidae | <i>Parapristipoma humile</i> Guinean grunt | Demersal | Crustaceans, Molluscs |
| Moronidae | <i>Dicentrarchus punctatus</i> Spotted seabass | Pelagic | Fish, Cephalopods, Crustaceans |
| Mugilidae | <i>Mugil cephalus</i> Flathead mullet | Benthopelagic | Zooplankton, benthic organisms and detritus |
| Mullidae | <i>Pseudupeneus prayensis</i> West African goatfish | Demersal | Benthic invertebrates, (mainly Bivalves) |
| Sciaenidae | <i>Argyrosomus regius</i> Meagre | Benthopelagic | Fishes and swimming Crustaceans |
| Serranidae | <i>Epinephelus marginatus</i> Dusky grouper | Reef- associated | Fish, Cephalopods, Crustaceans |
| Serranidae | <i>Cephalopholis taeniops</i> African Hind | Demersal | Fish |
| Serranidae | <i>Mycteroperca rubra</i> Mottled grouper | Demersal | Fish, Cephalopods |
| Soleidae | <i>Pegusa lascaris</i> Sand sole | Demersal | Bivalves, Crustaceans, Polychaetes |
| Sparidae | <i>Diplodus bellottii</i> Senegal seabream | Benthopelagic | Crustaceans and Molluscs |
| Sparidae | <i>Pagrus auriga</i> Redbanded seabream | Benthopelagic | Molluscs, Crustaceans |
| | <i>Pagrus caeruleostictus</i> Bluespotted seabream | Benthopelagic | Bivalves, Crustaceans, Fish |

Some high Cd values are recorded, such as 0.627 in female gonads of *Cephalopholis taeniops* and 0.990 $\mu\text{g g}^{-1}$ in male gonads of *Pagrus caeruleostictus* and ca 0.600 $\mu\text{g g}^{-1}$ in *Diplodus bellottii* (male and female). Mean copper concentrations in the muscle (Table 3 and Fig. 1) are ranging from 0.46 (*Argyrosomus regius*) to high values 6.99 $\mu\text{g g}^{-1}$ (*Pagrus auriga*). As for cadmium, gills generally present higher Cu concentrations than muscles with the highest recorded for 4.17 $\mu\text{g g}^{-1}$ in *Pseudupeneus prayensis*. Liver (Fig. 1) shows higher Cu concentrations than muscle and gills, particularly that of 85.14 in *Diplodus bellottii* and 117.37 $\mu\text{g g}^{-1}$ in *Dicentrarchus punctatus*. The lowest hepatic Cu concentrations are recorded in *Rhinobatos cemiculus* and *Cephalopholis taeniops* (ca 10 $\mu\text{g g}^{-1}$). Gonads (Fig. 1) have intermediate values, the lowest are found in *R. cemiculus* and *D. bellottii* (male : 1.78 $\mu\text{g Cu g}^{-1}$) and the highest in *D. punctatus* (female : 15.58 $\mu\text{g g}^{-1}$) and in *Pagrus caeruleostictus* (male : 52.06 $\mu\text{g g}^{-1}$).

Table 3. Metal concentrations ($\mu\text{g g}^{-1}$ dry wt) in the muscles and gills in bony fish (N.D. = not determined).

| Species/organ | Tissue | Cd ($\mu\text{g/g}$) | Cu ($\mu\text{g/g}$) | Zn ($\mu\text{g/g}$) |
|---|--------|------------------------|------------------------|------------------------|
| <i>Mugil cephalus</i> n = 1 | Muscle | 0.110 | 1.16 | 14.16 |
| | Gills | 0.053 | 1.57 | 50.72 |
| <i>Pseudupaeneus prayensis</i> n = 4 | Muscle | 0.066 \pm 0.054 | 1.04 \pm 0.06 | 8.92 \pm 1.94 |
| | Gills | 0.272 \pm 0.060 | 4.17 \pm 0.19 | 67.53 \pm 27.51 |
| <i>Parapristipom latifrons</i> n = 3 | Muscle | 0.084 \pm 0.013 | 1.89 \pm 0.45 | 10.12 \pm 2.00 |
| | Gills | 0.084 \pm 0.046 | 1.76 \pm 0.26 | 46.78 \pm 8.22 |
| <i>Argyrosomus regius</i> n = 3 | Muscle | 0.005 \pm 0.005 | 0.46 \pm 0.01 | 8.63 \pm 1.17 |
| | Gills | N.D. | N.D. | N.D. |
| <i>Epinephelus marginatus</i> n = 1 | Muscle | 0.168 | 1.14 | 15.85 |
| | Gills | 0.051 | 1.12 | 64.69 |
| <i>Myxeroperca rubra</i> n = 4 | Muscle | 0.051 \pm 0.016 | 0.72 \pm 0.16 | 11.22 \pm 1.98 |
| | Gills | 0.060 \pm 0.033 | 1.29 \pm 0.40 | 67.34 \pm 13.29 |
| <i>Pegusa lascaris</i> n = 3 | Muscle | 0.273 \pm 0.133 | 0.89 \pm 0.04 | 15.05 \pm 2.36 |
| | Gills | N.D. | N.D. | N.D. |
| <i>Pagrus auriga</i> n = 2 | Muscle | 0.040 \pm 0.025 | 6.99 \pm 0.74 | 7.73 \pm 1.92 |
| | Gills | 0.313 \pm 0.095 | 9.57 \pm 2.21 | 32.63 \pm 15.42 |

Mean zinc concentrations in the muscle (Table 3 and Fig. 1) are ranging from 7.73 (*Pagrus auriga*) to 15.85 $\mu\text{g g}^{-1}$ (*Epinephelus marginatus*). As for cadmium and copper, gills concentrate zinc from 32.63 (*P. auriga*) to 105.39 $\mu\text{g g}^{-1}$ (*Diplodus bellottii*) compared to the muscles. Liver (Fig. 1) has higher values than muscle and gills to some extent. For instance, values range from 34.41 in *Rhinobatos cemiculus*, 160.32 in *Pagrus caeruleostictus* and 207.87 $\mu\text{g g}^{-1}$ in *Diplodus bellottii*. Zinc is particularly concentrated in gonads (Fig. 1), especially in females from *D. bellottii* (948.57 $\mu\text{g g}^{-1}$) and *P. caeruleostictus* (1463.14 $\mu\text{g g}^{-1}$).

The distribution of metals among tissues is not exactly the same according to the considered metal. Concentrations are higher in the gills and especially in the liver compared to the muscle. There is no difference among males and females in the metal concentrations of muscle, gills and liver. The concentrations in the muscle are below the proposed limit values for human consumption of fish which are 0.5 $\mu\text{g Cd g}^{-1}$ dry wt. (CSHPF 1995), 150 $\mu\text{g Cu g}^{-1}$ and 5 mg Zn g^{-1} according the National Health Medical Research Council of Australia (*in* Bebbington et al. 1977).

The concentrations of metals in gills reflect the concentrations of metals in the waters, where the fish species lives ; they are higher than those in the muscles due to the high volume of filtered seawater. The concentrations in liver represent storage of metals. Induction of metallothioneins MTs in the liver is the main form of storage and detoxication of metals in fish (Hamilton and Mehrle 1986 ; Filipović and Raspor 2003).

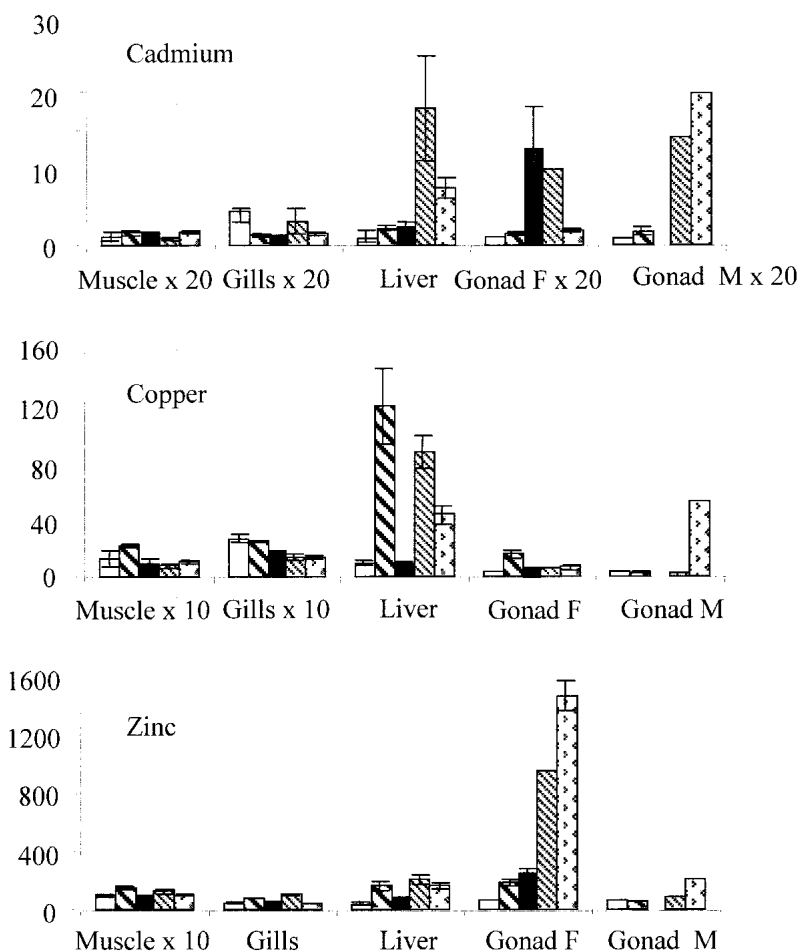


Figure 1. Concentrations ($\mu\text{g g}^{-1}$ dry wt) in *Rhinobatos cemiculus* \square ($n = 3$, one female, one male, one fish of undetermined sex), *Dicentrarchus punctatus* ▤ ($n = 7$ with 3 females and 4 males), *Cephalopholis taeniops* \blacksquare ($n = 10$ females, only one female gonad could be analyzed), *Diplodus bellottii* ▨ ($n = 2$ with 1 male and 1 female), *Pagrus caeruleostictus* ▤ ($n = 6$ with 3 males and 3 females).

Cadmium is nearly 100-fold higher in the liver than in the muscle whereas copper is between 10 and 100-fold higher. Zinc seems less enriched in the liver than the two other metals with an increase of 10 to 20.

The problem of higher cadmium concentrations in all tissues, and particularly in livers of fish collected from the Mauritania coast, must be underlined. Data from the literature showed that the cadmium concentrations in the liver of various

species are less than $10 \mu\text{g g}^{-1}$ dry wt and more particularly less than $1 \mu\text{g g}^{-1}$ (Hamza-Chaffai et al. 1996 ; Roméo et al. 2000a). Hepatic Cd concentrations are higher than $1 \mu\text{g g}^{-1}$ in all the bony fish shown in Fig. 1. Cadmium could originate from water, sediment and food. High levels of cadmium were already found in the livers of fish collected in the same area (Roméo et al. 1999). These levels were attributed by the authors to natural origin, such as the upwelling of deep waters which takes place along the Western Atlantic coast. Bruland and Franks (1983) showed that Cd but also Zn have nutrient-type distributions in Atlantic waters, dissolved cadmium being correlated with phosphate concentrations in sea water. Moreover, phosphate rocks are very common in Mauritania but also in Senegal which extracts and exports this fertiliser. Waters from Senegal follow a current which reaches the coast of Nouakchott (Margalef 1975). Leaching of phosphate rocks may increase phosphate concentrations of waters. Bustamante et al. 2003 found the same range of cadmium concentrations in the livers of pelagic and benthic fish from sub-Antarctic Archipelago of Kerguelen and observed that these concentrations tend to be higher than those reported in the current literature. The authors suggested that the occurrence of upwelling of deep waters in the Kerguelen region should bring an enrichment of Cd in the surface waters.

Copper hepatic concentrations in fish reported in the literature are highly variable. Values ranging from 8 to $20 \mu\text{g g}^{-1}$ were reported in the livers of Serranidae (*Serranus scriba*, *Cephalopholis nigri*), and the Mullidae *Pseudupeneus prayensis*, collected in the same area (Roméo et al. 1999). This is in agreement with concentrations measured here in the livers of the Serranidae *Cephalopholis taeniops* and the cartilaginous fish *Rhinobatos cemiculus* (Fig. 1). In these species, copper appears to be under close physiological regulation as generally stated for this essential metal (Thompson 1990). Higher copper values recorded by some authors may indicate a preferential storage in this organ. A high hepatic copper storage ($1000 \mu\text{g g}^{-1}$), related to a high hepatic metallothionein level, was found in a teleost fish *Morone americana* (Moronidae) by Bunton et al. (1987). In this study, the highest value was found in *Dicentrarchus punctatus* which also belongs to Moronidae.

Gonads seem to be particularly rich in cadmium and zinc, the enrichment for zinc may be explained by the well-known physiological role of zinc in fertilization. Julshamn and Braekkan (1976) found that the zinc level in the ovary of the cod was higher than in any other organ of the fish. Moreover, juvenile cod roe was found to have 3 times more zinc than mature cod roe (Julshamn et al. 1978). Cadmium is often associated with zinc. Eisler and Gardner (1973) found synergy in the metal accumulation of cadmium and zinc in the fish *Fundulus heteroclitus*.

The species which appear to store the highest concentrations of cadmium, copper and, to a less extent, zinc are the pelagic fish *Dicentrarchus punctatus* (eating on fish, crustaceans and cephalopods) and the bathopelagic fish *Diplodus bellottii* and *Pagrus caeruleostictus* eating on crustaceans and molluscs (Table 2). Cephalopods are susceptible to present high levels of cadmium and act as vectors of the transfer of cadmium to top marine predators in the Atlantic (Bustamante et

al. 1998). In the Mauritania coast, molluscs are known to present high metal and especially cadmium concentrations (Roméo and Gnassia-Barelli 1988, Sidoumou 1991, Roméo et al. 2000b).

A comparison with already published data on certain fish species from the Mauritania coast (Roméo et al. 1999) shows the same tendency for metal distribution in the different tissues and the same range of concentrations.

Both habitat and feeding habits influenced metal concentrations in fish in this study. Along the North-Western African coast, some high metal levels, especially cadmium, were found in tissues of fish such as livers and gonads which are occasionally consumed by man. These levels may be above the proposed limits for human consumption but these considered tissues are eaten in much lower quantities than muscles.

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