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Content of Lead and Cadmium in Barred Hogfish, *Bodianus scrofa*, Island Grouper, *Mycteroperca fusca*, and Portuguese Dogfish, *Centroscymnus coelolepis*, from Canary Islands, Spain

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Abstract Concentration of lead and cadmium has been analyzed in *Bodianus scrofa* and *Mycteroperca fusca* captured in the Canary Islands coast. Concentration of Pb ranged from 2.53 to 306.40 and 4.97 to 792.00 μg kg^{-1} respectively, while that of Cd ranged from 1.75 to 1854.50 and 6.78 to 656.00 μg kg^{-1}. The same metals have been analyzed in muscles, liver and skin of *Centroscymnus coelolepis* from Canary Islands, with contents of Pb and Cd ranged between 24.18–96.12 μg kg^{-1} and 32.00–3266.58 μg kg^{-1} respectively, and in the Azores Archipelago, with concentrations of Pb and Cd ranged as follow: 18.41–38.99 μg kg^{-1} and 5.23–4179.87 μg kg^{-1} respectively. Percentage of contribution of both metals to the PTWIs, has also been calculated for both fishes.

Keywords Heavy metals · Bony fish · Sharks · Canary Islands

Due to the importance of marine ecosystems and human living, the effects of pollution constitute the center of interest in marine research. Heavy metals naturally occur in seawater in very low concentrations, but the grow of global population and industrial development have increased the marine contamination of heavy metals (Yilmaz and Yilmaz 2007; Franca et al. 2005).

Effects of heavy metals on marine communities, where accumulation and concentration can occur through trophic chains, have been studied. Several species, like fishes, have been used as indicators, because they serve for long term monitoring of metal accumulation in the marine environment (Tüzen 2003; Coğun et al. 2006). Food and feeding habits are factors which affect metal concentration (Roméo et al. 1999); its position in the food chain has been considered of great importance in some cases. Some marine organisms can contain higher levels of certain metals than levels found in the surrounding environment, because they can absorb metals from food, suspended matter, or directly from seawater (Hashmi et al. 2002).

For this study, these two coastal osteichthyes species were chosen for several reasons: because of the high captures in the Canary Islands, they stay in the same habitat, do not migrate appreciatively and both species are used as indicators of overfishing in this area (Franquet and Brito 1995); Some decades ago(in the 50s and 60s) deep-see sharks (chondrichthyes) were an important fishery resource in the Canary Islands and catches constituted a large quantity in the medium-scale fisheries of the three western islands of the archipelago (Tenerife, La Palma and La Gomera). The high amount of livers of these species (at least 75% of liver comes from dogfishes), their high levels of protein (near 23%) associated to very low levels of lipids (under 0.8%) make these species be good edibles for human beings (Brito et al. 1998; Lozano et al. 1999). For all these reasons and the fact that bibliography shows many references of this type of study worldwide but not in the Canary Islands or Spanish coasts, the aims of this study

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were to analyze and compare the levels of Pb and Cd in three species *Bodianus scrofa*, *Mycteroperca fusca* and *Centroscymnus coelolepis*, present in the Canary Islands coast.

Materials and Methods

Samples

A total amount of 28 samples of *B. scrofa* (Valenciennes, 1839) and 21 of *M. fusca* (Lowe, 1838) were collected from commercial fisheries in the coast of La Graciosa (Lanzarote, NE of Canary Islands) by hook-and-line at 5–50 m depth, during a period of 2 years. Their whole stomach and content were weighted, washed and filtered, and food items were separated and determined in a binocular lens (Leica Zoom 2000™), and subsequently classified according to the taxon of the possible lowest level. In the same way, 20 specimens of Portuguese dogfishes *C. coelolepis* (Bocage and Capello, 1864) were collected from scientific fisheries at 700–1,500 m depth in the Canary Islands in several cruises along the south west coast of Tenerife. In the case of specimens from Azores (17 specimens), samples were removed on board N/I Archipelago (research ship belonging to the University of Azores) during short cruises in La Graciosa, Saint George and Teixeira Islands at 800–1,200 m depth.

Determination of Metals

Ten gram of each homogenized sample were place in porcelain crucibles and dried on a hot plate from 60 to 80°C for at least 12 h. The crucibles with the samples were then introduced in muffle ovens and burned to ash at 425°C. The white ashes obtained with this procedure were then dissolved in 1.5% nitric acid. Measurements were performed with a Perkin-Elmer 4100 ZL AAS with a Graphite Perkin-Elmer 4100 ZL furnace and Automatic Sampler Perkin-Elmer AS 70. In the lead and cadmium analyses, a mixture of $NH_4H_2PO_4$ and $Mg(NO_3)_2$ were used as matrix modifiers. The detection limits, calculated as three times the standard deviation of 15 blanks for the acid digest, were 0.28 and 0.065 μg L^{-1} for lead and cadmium respectively. Table 1 presents the temperature program of the graphite furnace for Pb and Cd.

Quality control of the analytical measurements was performed using blank samples and the following reference materials: Pb: NBS SRH 1577a Bovine Liver, and Cd: BCR CRM 184 Bovine Muscle for bony fish, and for Portuguese dogfish: Pb: DORM-2 (Dogfish Muscle Reference Material); Cd: DOLT-2 (Dogfish Liver Reference Material). All obtained results were very similar to Certified Values of these materials and confirmed suitability of our procedures and methodology (Table 2) as previously done by us (Gutiérrez et al. 2004).

Table 1 Thermal programme used for the determination of lead and cadmium in the graphite furnace

Phase	Temperature (°C)	Rise time (s)	Hold time (s)	Argon flux (mL/min)
Evaporation	100	10	20	250
Drying	130	25	20	250
Pirolysis	450	15	20	250
Pre-treatment	800[a] 700[b]	5	10[c] 5[d]	250
Atomisation	1,250	0	3	0
Cleaning	2,500	2	3	250

Injection temperature: 20°C; Wavelength of the Pb: 283,3 nm; Wavelength of the Cd: 228,8 nm; Volume of the injection: 20 μL

[a] Pre-treatment temperature for the Pb

[b] Pre-treatment temperature for the Cd

[c] Time at which the temperature for the pre-treatment of the Pb is maintained

[d] Time at which the temperature for the pre-treatment of the Cd is maintained

Table 2 Reference materials recovery study

Metal	Reference material	Obtained values (μg kg^{-1})	Certified values (μg kg^{-1})	n
Pb	NBS SRH 1577a	134 ± 17	135 ± 15	10
Pb	DORM-2	68.2 ± 0.98	65 ± 7.0	10
Pb	DOLT-2	230.2 ± 18.1	220.0 ± 20.0	10
Cd	BCR CRM 184	12.0 ± 1.0	13.0 ± 2.0	10
Cd	DORM-2	49.36 ± 2.09	43.0 ± 8.0	10
Cd	DOLT-2	20150.0 ± 450.0	20800.0 ± 500.0	10

n Number of samples

Statistical Analysis

The statistical analysis of the obtained results consisted in a first Kolmogorov–Smirnov normality test and Shapiro-Wilk, followed by the study of the variance homogeneity using an ANOVA parametric test with a DMS post hoc and Tukey HSD test.

Results and Discussion

The levels of heavy metals found in different tissues of *B. scrofa* and *M. fusca* are shown in Table 3. Regarding Pb and Cd in *B. scrofa*, the spleen contained the highest level of Pb followed by the kidneys and liver, whereas regarding

Table 3 Concentrations of Pb and Cd (Median value ± Standard deviation) in various tissues of *B. scrofa* and *M. fusca*

Species	Tissue	n	Pb (μg kg^{-1} wet weight)	n	Cd (μg kg^{-1} wet weight)
B. scrofa	Brain	1	58.00	1	52.00
	Gills	9	158.14 ± 150.90	8	67.80 ± 57.63
	Heart	2	43.15 ± 9.90	2	392.60 ± 19.70
	Kidneys	6	180.90 ± 166.80	6	804.50 ± 376.40
	Liver	13	173.90 ± 283.60	12	1854.50 ± 1111.0
	Muscle	13	47.09 ± 36.49	11	7.95 ± 5.84
	Skin	3	34.80 ± 60.30	2	1.75 ± 2.40
	Spleen	11	306.40 ± 266.00	10	461.40 ± 571.40
	Vertebrae	3	2.53 ± 2.60	3	14.53 ± 22.20
M. fusca	Brain	3	792.00 ± 983.30	3	65.00 ± 91.03
	Gills	11	416.90 ± 539.40	11	6.78 ± 11.10
	Heart	11	83.40 ± 59.30	11	73.75 ± 38.84
	Kidneys	10	62.15 ± 54.58	10	113.78 ± 1297.6
	Liver	16	109.10 ± 135.30	16	656.00 ± 922.80
	Muscle	18	65.70 ± 104.90	19	10.70 ± 7.93
	Skin	3	134.90 ± 195.00	3	10.87 ± 7.43
	Spleen	2	360.00 ± 279.30	2	440.50 ± 143.54
	Vertebrae	17	4.97 ± 8.53	17	23.34 ± 58.35

n Number of samples

Cd the liver presented the highest level followed by the kidneys. Regarding *M. fusca*, the highest content of Pb was found in the brain followed by the gills, while the liver presented the highest level of Cd followed by the spleen. In both species liver tissue appears to be a major storage site for heavy metals. Therefore in the liver, metal concentrations may be reflective of recent accumulation and may be useful indicator of recent exposure (Coğun et al. 2006). This also is probably due to the physiological role of the liver in fish metabolism. It has been shown that target tissues of heavy metals are metabolically active ones, such as the liver, the kidneys and the gills, as compared to the low-metabolism tissues like muscle (Filazi et al. 2003).

In general, in muscle and skin compared to gills, liver and kidneys, metal concentrations were lower and this is important, because muscle and skin constitute the greatest consumed mass of the fish.

The bioaccumulation of the studied heavy metals is different depending of the species. Higher levels of Pb were found in *M. fusca* compared with that of *B. scrofa*, whereas regarding cadmium higher levels were found in *B. scrofa*. These differences may be a result of different age, size, metabolic activity and feeding habits of the studied species and in this case, probably the differences between species are due to feeding habits differences: *B. scrofa* is a predator on benthic invertebrates and *M. fusca* is a typical predator on planktofagous and microbenthofagous fish.

Data obtained on the Pb and Cd concentrations in island grouper and barred hogfish do not show inordinately high levels in muscle tissue (Pb: *B. scrofa*: 47.90 ± 36.49 μg kg^{-1} ww, and *M. fusca*: 65.70 ± 104.90 μg kg^{-1} ww; Cd: *B. scrofa*: 7.95 ± 5.84 μg kg^{-1} ww, and *M. fusca*: 10.70 ± 7.93 μg kg^{-1} ww). Metal concentrations are much lower than the maximum permissible levels for human consumption established by European Commission Regulation 2006/1881/CE for Pb (300 μg kg^{-1} ww) and Cd (50 μg kg^{-1} ww). Therefore levels found in muscle tissue indicate that consumers of these fish have no risk of contamination of Pb and Cd.

Otherwise, in the case of Portuguese dogfish of Canary Islands and Azores specimens, as it can be observed in Table 4, Pb and Cd maximum values were obtained in liver, followed by those found in muscles. These differences could be explained because concentrations of metals in muscles reflect content of metals in the waters, where the fish species lives, whereas the concentrations in liver represent storage of metals (Tepe et al. 2008). On the contrary, the minimum values of the studied metals were found in the skin. It can be observed that the highest level of Pb from Canary Islands and Açores was found in liver of Canary Islands specimens, and the highest level of Cd was obtained in liver from Açorean specimens.

Significant differences in Pb concentrations in liver and skin, and in Cd concentrations in skin between Canary Islands and Azores were observed ($p < 0.05$).

The results of this study are very similar to those shown by Hardisson et al. (1997) for this species in deep-sea waters of Tenerife (Canary Islands).

As occurred in the two previous mentioned species, all data obtained on Pb concentrations in *C. coelolepis* from these two macaronesian archipelagos show no non-ordinary high levels in muscle tissue. In this case metal concentrations also are very well below the maximum permissible levels for human consumption as established by European Commission Regulation 2006/1881/CE. Regarding Cd it can be observed that levels in muscle tissue from Azores specimens are close the maximum

Table 4 Concentrations of Pb and Cd (median value ± standard deviation) in three tissues of *Centroscymnus coelolepis* of each area

Area	Tissue	n	Pb (μg kg^{-1} wet weight)	n	Cd (μg kg^{-1} wet weight)
Canaries	Liver	18	96.12 ± 106.83	18	3266.58 ± 4256.59
	Muscle	20	51.03 ± 33.08	20	60.21 ± 72.49
	Skin	19	24.18 ± 37.75	19	32.00 ± 60.81
Açores	Liver	13	38.99 ± 30.46	13	4179.87 ± 30.46
	Muscle	15	32.67 ± 11.93	15	45.39 ± 44.25
	Skin	8	18.41 ± 8.52	8	5.23 ± 9.59

n Number of samples

permissible levels for human consumption (50 μg kg^{-1} ww), whereas muscle tissue of species of the Canary Islands are over the maximum permitted.

On the other hand, bioaccumulation is different depending on the area. Higher levels of Pb were found in specimens from Canary Islands compared with those of Azores, whereas regarding Cd higher levels were found in Azores: despite of having less Cd in muscles and skin, they have higher levels of this metal in the liver.

As a mean, consumption of 45.8 g of fish per person and day is considered for the Canarian population, the contribution of the daily intake of fish to the Provisional Tolerable Weekly Intakes (PTWIs) fixed by the WHO for Pb and Cd (WHO 1993) should be taken into account. Considering the median content of Pb and Cd in muscle of *B. scrofa*, *M. fusca* and *C. coelolepis* from Canary Islands and the mean consumption of fish per person and day for the Canarian population, the contribution of these metals to the Provisional Tolerable Weekly Intakes (PTWIs) are irrelevant being 2.501 μg Pb day^{-1} (17.51 μg Pb $week^{-1}$) and 1.204 μg Cd day^{-1} (8.428 μg Cd $week^{-1}$). This represents, for an average person weighting 65 kg, approximately 1.078% of the PTWI in the case of Pb and 1.852% for Cd. Nevertheless, it should be taken into account that there are other sources of these metals to the diet.

In conclusion, researches carried out in the present study provide information about lead and cadmium contents in *B. scrofa*, *M. fusca* and *C. coelolepis* from Canary Islands coast and indirectly indicate the environmental contamination along the coastal areas. The studied metals measured in the fishes that have been analyzed in this study, are below the legal limits established by the current legislation except for muscle tissue of *C. coelolepis* from Canarian species. In addition, the results of this study show that there do exist needs to evaluate and monitor lead and cadmium levels in fishes to establish the intake values which are safe for the population and that the study of content of these metals can be used as good indicators for the long term monitoring of metal accumulation in the marine environment.

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