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Trace metals in tissues of *Galeus melastomus* Rafinesque, 1810 from the northern Tyrrhenian Sea (NW Mediterranean)

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In the last decades, the decline of coastal waters resources has forced fisheries to expand into deeper waters. However, while the increase of industrial activities make it essential to find biological models that can explain pollutants dynamics, little is still known about pollutants distribution, dynamics, and their possible effects on deep-water organisms. In this context, new information on the concentrations of trace metals (Arsenic, As; Cadmium, Cd; Copper, Cu; Mercury, Hg; Lead, Pb) in muscle, liver and gonads of blackmouth catshark, Galeus melastomus*, from north-western Mediterranean (northern Tyrrhenian Sea) are presented. Significant differences between males and females were found in the concentrations of three of the five trace elements in gonads. Lower concentrations of trace metals were found in the ovaries, and this could be due to the almost continuous vitellogenic activity which could transfer contaminants to developing oocytes.*

Key words: trace elements, deep waters, *Galeus melastomus*, Tyrrhenian Sea

INTRODUCTION

Up to the last decade bioaccumulation studies concentrated on coastal species, however little is still known about pollutants distribution and their possible effects on organisms in deep-water environments.

The blackmouth catshark, *Galeus melastomus* Rafinesque, 1810 (Elasmobranchii, Triakidae), is a deep-water species distributed along the eastern Atlantic coast and in the Mediterranean basin. It shows a wide bathymetric range (100-1500 m depth), but it is more abundant on muddy bottoms from 300 to 800 m depth (OLASO *et al.*, 2004; SION *et al.*, 2004; ORDINES *et al.*, 2011). Although, it is of low commercial value, *G. melastomus* is a by-catch species in the Mediterranean bottom trawl fishery targeting Norway lobster (*Nephrops norvegicus*), red shrimps (*Aristaeomorpha foliacea* and *Aristeus antennatus*), and deep-water rose shrimp (*Parapenaeus longirostris*) (SBRANA *et al.*, 2003; SION *et al.*, 2004;

ORDINES *et al.*, 2011; LIGAS *et al.*, 2013). Therefore, the blackmouth catshark could be considered a good bio-indicator organism to predict heavy metals accumulation in deep-water demersal communities, due to its nekton-benthic behavior, its wide bathymetric distribution range, and the potential effects on human consumption.

In the present paper new information on the concentrations of trace metals (Arsenic, As; Cadmium, Cd; Copper, Cu; Mercury,Hg; Lead, Pb) in tissues of *G. melastomus* caught in the northern Tyrrhenian Sea (NW Mediterranean) are presented.

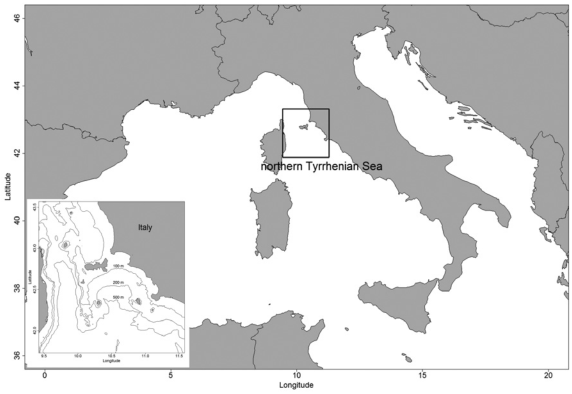

Fig. 1. Map of the investigated area (northern Tyrrhenian Sea); 100, 200 and 500 m isobaths are also shown

MATERIAL AND METHODS

Blackmouth catshark specimens were caught in April 2012 in the northern Tyrrhenian Sea (Fig. 1) by commercial trawl vessels fishing at depths between 300 and 500 m; the area represents an important fishing ground for the trawl fleet targeting *Nephrops norvegicus* and *Parapenaeus longirostris* (SBRANA *et al.*, 2003).

Only commercial-sized specimens were retained (specimens < 40 cm were discarded); all the specimens collected were measured (total length, TL, cm), weighed (wet weight, g), and sexed. Portion of muscle tissue (5 g) from the area near the dorsal fin, liver and gonad samples (5 g each) were collected and stored at –24°C for chemical analyses. Samples were dried to constant weight at 45±1 °C for 48 h, digested with 5 ml of nitric acid and 2 ml of hydrogen peroxide using a microwave digestion system (10 min to reach 180°C, 10 min at 180°C, US EPA 3052 modified), and diluted with ultra-pure water to a final volume of 25 ml. Blank samples (reagents only) were processed using the same procedure. Total metals concentration was determined by atomic absorption spectrometry with graphite furnace atomization and Zeeman's effect (SpectrAA-220 Zeeman, Varian, Mulgrave, Victoria, Australia). Hg level was measured on whole undigested tissue (liver, muscle and gonads) with LECO AMA 254 Advanced Mercury Analyzer. The accuracy of the analysis was checked using a standard reference material (ERM-CE278 – Mussel tissue, Central Institute for Reference Materials and Measurements, Belgium, and QUASIMEME material, QTM093BT Hake whole tissue).

A Kolmogorov-Smirnov non-parametric test was applied to investigate the difference in concentration of the metals in the various tissues between males and females. Data analyses were carried out using the package R 2.15.2 (R CORE TEAM, 2012; www.r-project.org). A significance level of 5% was used in all the statistical analyses.

RESULTS AND DISCUSSION

A total of 34 commercial-sized blackmouth catshark specimens were collected; males (24 specimens) ranged from 40.5 to 48.0 cm TL in size and from 152 to 312 g in weight, while females (10 specimens) from 44.5 to 50.0 cm TL and from 251 to 353 g (Table 1).

Mean metal concentrations expressed on a dry weight basis are summarized in Table 2 (mean ± standard deviation). Significant differences between males and females were found by means of the Kolmogorov-Smirnov non-parametric test in the concentrations of Cu, Hg, and Pb in gonadal tissues (Table 3). Gonadal activity could play an important role in bioaccumulation process. In fact, in *Galeus melastomus* the vitellogenic activity is constant all year round (COSTA *et al.*, 2005) and this could produce a dilution effect on female gonads. As suggested by different authors (MINGANTI *et al.*, 1996; BODIGUEL *et al.*, 2009; KOENIG *et al.,* 2013), the lower levels of metals in females have been reported in differ-

Table 1. Morphometric characteristic of the 34 specimens of Galeus melastomus *used for the analysis*

n. specimen	Total Length (cm)	Weight (g)	Sex
1	44.5	251	F
2	45.0	275	F
3	45.5	294	F
4	46.0	250	F
5	46.5	263	F
6	46.5	306	F
7	47.0	290	F
8	48.0	308	F
9	48.0	328	F
10	50.0	353	F
11	40.5	152	M
12	41.0	249	M
13	41.0	213	M
14	42.0	211	M
15	42.0	207	M
16	43.0	217	M
17	43.0	208	M
18	43.0	201	M
19	43.0	229	M
20	43.5	232	M
21	43.5	241	M
22	43.5	219	M
23	43.5	208	M
24	44.0	230	M
25	44.0	235	M
26	44.0	237	M
27	44.5	242	M
28	44.5	224	M
29	44.5	262	M
30	45.0	235	M
31	45.5	255	M
32	46.0	253	M
33	47.0	312	M
34	48.0	268	M

Table 3. Summary of the results of the Kolmogorov-Smirnov *non-parametric test used to investigate the difference between sexes of trace metal concentration in the various tissues; ns = not significant; * = $p < 0.05$*

	Tissue		
	Muscle	Liver	Gonads
As	ns	ns	ns
Cu	ns	ns	*
Hg	ns	ns	*
Cd	ns	ns	ns
Pb	ns	ns	*

ent species and it could be explained by variation of biological parameters between males and females, such as energy investment in reproduction investment, size at first maturity, cost of gametes synthesis or transfer of contaminants to developing oocytes.

To allow the comparison of values measured in this study with European Regulatory data for human consumption and safety (EUROPEAN COMMISSION Dir. 2003/100/CE; EUROPEAN COMMISSION Reg. CE n. 1881/2006), data obtained regarding concentrations of metals in muscle have been converted to concentration on wet weight according to the equation:

$$WW = DW \times [1 - (WP)]$$

where WW is wet weight concentrations, DW is dry weight concentration and WP is the water percentage in muscles measured in this experiment (74%).

While all the metals analyzed showed concentrations in the muscles of *G. melastomus*

Table 2. Mean concentrations (± standard deviation) of As, Cd, Cu, Hg, Pb (µg g-1 dry weight) in Galeus melastomus *tissues. The numbers of specimens analyzed is also shown*

Males (N = 24)					
Tissue	**As**	**Cu**	**Hg**	**Cd**	**Pb**
Muscle	156.5 ± 58.5	1.6 ± 0.5	9.2 ± 3.5	0.1 ± 0.0	0.3 ± 0.2
Liver	107.5 ± 65.4	8.2 ± 3.6	4.0 ± 2.3	2.9 ± 1.1	3.7 ± 1.8
Gonads	82.5 ± 28.4	15.2 ± 5.5	6.9 ± 2.9	0.9 ± 0.5	1.3 ± 0.6
Females (N = 10)					
Tissue	**As**	**Cu**	**Hg**	**Cd**	**Pb**
Muscle	192.5 ± 23.3	1.8 ± 1.2	12.5 ± 4.2	0.1 ± 0.0	0.4 ± 0.2
Liver	101.6 ± 66.1	9.9 ± 4.5	4.1 ± 2.9	2.9 ± 1.4	3.2 ± 1.9
Gonads	42.1 ± 10.7	3.6 ± 1.2	1.7 ± 1.1	0.5 ± 0.2	0.4 ± 0.2

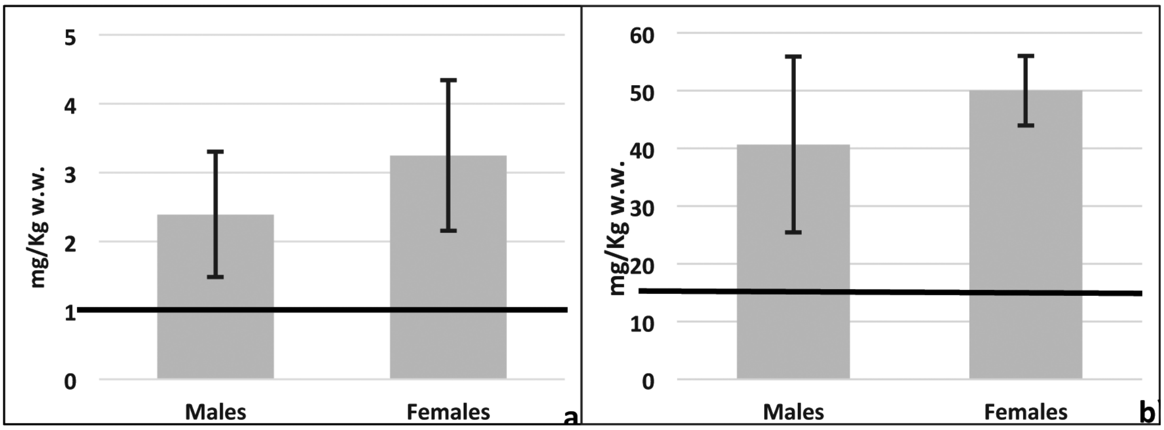

Fig. 2. Mercury (a) and Arsenic (b) wet weight concentrations (w.w.) in males and females of G. melastomus *exceeding the European Regulatory levels of 1mg/Kg w.w. and 15 mg/Kg w.w. respectively (solid lines)*

from the northern Tyrrhenian Sea below regulatory limits, particularly high values of As and Hg were observed, exceeding the indicated limit and therefore posing a potential risk for human consumption (Fig. 2). This remarkable level of bioaccumulation in deep sea species has been previously described in literature in the Mediterranean and mainly ascribed to the high trophic level and long life related with species inhabiting this environment (STORELLI *et al.,* 1998; BODIGUEL *et al.*, 2009; KOENIG *et al.,* 2013). Indeed, stable isotope analysis demonstrated that the mean trophic level of some shark species, including *G. melastomus*, is similar to other top predators such as marine mammals whose bioaccumulation is well demonstrated (DOMI *et al.*, 2005).

As concerns Hg, the observed values are slightly higher than those reported by HORNUNG *et al.* (1993) and STORELLI *et al.* (2002, 2011) in *G. melastomus* from other areas of the Mediterranean Sea and by VAS (1991) from the Atlantic. Also Cu levels found in the present work are higher than those reported by HORNUNG *et al.* (1993) from the eastern Mediterranean Sea.

These high levels of trace metals concentration may be due to the geochemical anomalies that characterize the investigated area and are the results of two synergic factors: natural origins and mining industries impact (BARGHIGIANI *et al.*, 1996; LEONI & SARTORI, 1996; LOPPI, 2001). It is known that the river basins, aquifer and soil in the investigated area have been affected by peculiar land contamination that could have acted as potential source of input and diffusion of toxic elements (Cd, Hg, Pb) also in the marine environment (LOPPI, 2001).

BARGHIGIANI *et al.* (1996) analyzing marine sediments and cores collected in the northern Tyrrhenian Sea found the highest concentration of Hg in the < 20µm grain-size fraction of coastal sediments (0.71 $\mu g\ g^{-1}$ dry weight), which indicated transport of mercury from the land to the sea by the rivers. However, they also observed that Hg concentrations were showing a decreasing trend from the coast towards off-shore areas. Therefore, being the investigated species mainly distributed in deep-waters, the high concentrations of metals found in tissues of *G. melastomus* may represent an issue of great concern, and stress the need for further investigations aimed at deepening the knowledge on the still poorly known heavy metals dynamics in deep-water ecosystems (MATHEWS & FISHER, 2009), and the potential effects on human consumption.

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Tragovi metala u tkivima *Galeus melastomus* (Rafinesque, 1810) iz sjevernog dijela Tirenskog mora (SZ Mediteran)

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SAŽETAK

Pad resursa u obalnim vodama u posljednjih nekoliko desetljeća prisilio je ribarstvo da se proširi i na dublje vode. Međutim, dok je zbog porasta industrijskih aktivnosti bitno pronaći biološke modele koji mogu objasniti dinamiku zagađivala, malo se zna o njihovoj distribuciji i dinamici te o njihovim mogućim učincima na dubokomorske organizme. U tom kontekstu, prikazane su nove informacije o koncentraciji tragova metala (arsen, As; kadmij, Cd; bakar, Cu; živa, Hg; olovo, Pb) u mišićima, jetrima i gonadama mačke crnouste, *Galeus melastomus,* iz sjeverozapadnog Mediterana (sjever Tirenskog mora). Značajne razlike između mužjaka i ženki uočene su u koncentracijama od tri do pet elemenata u tragovima u gonadama. Niže koncentracije tragova metala pronađene su u jajnicima, što bi mogao biti rezultat gotovo neprekidne vitelogene aktivnosti koja može dovesti do prenošenja zagađivala do oocita u razvoju.

Ključne riječi: elementi u tragovima, duboke vode, *Galeus melastomus*, Tirensko more