

# Distribution of trace elements in the tissues of smooth hound *Mustelus mustelus* (Linnaeus, 1758) from the southern–eastern waters of Mediterranean Sea (Italy)

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**Abstract** Trace element concentrations (Hg, Cd, Pb, Cr, Ni, Cu, Zn) were determined in the muscle, gonads, skin, and brain of smooth hound *Mustelus mustelus* in order to define the metal distribution patterns. The data indicated that metal accumulation depended on the tissues probably as a consequence of metabolic needs, physicochemical properties, and detoxification processes specific for each element. Metal concentrations were higher in gonads (Hg 0.10–0.70  $\mu\text{g g}^{-1}$ ; Cd 0.02–0.10  $\mu\text{g g}^{-1}$ ; Pb 0.08–0.39  $\mu\text{g g}^{-1}$ ; Cr 0.06–0.36  $\mu\text{g g}^{-1}$ ; Ni 1.37–3.00  $\mu\text{g g}^{-1}$ ; Zn 9.15–16.30  $\mu\text{g g}^{-1}$ ; Cu 1.95–21.62  $\mu\text{g g}^{-1}$ ) and skin (Hg 0.16–0.66  $\mu\text{g g}^{-1}$ ; Cd 0.01–0.04  $\mu\text{g g}^{-1}$ ; Pb 0.10–0.62  $\mu\text{g g}^{-1}$ ; Cr 0.15–0.68  $\mu\text{g g}^{-1}$ ; Ni 1.60–7.20  $\mu\text{g g}^{-1}$ ; Zn 9.00–16.00  $\mu\text{g g}^{-1}$ ; Cu 0.78–6.80  $\mu\text{g g}^{-1}$ ) than brain (Hg 0.04–0.34  $\mu\text{g g}^{-1}$ ; Cd 0.01–0.05  $\mu\text{g g}^{-1}$ ; Pb 0.03–0.59  $\mu\text{g g}^{-1}$ ; Cr 0.08–0.48  $\mu\text{g g}^{-1}$ ; Ni 5.59–9.69  $\mu\text{g g}^{-1}$ ; Zn 5.90–7.35  $\mu\text{g g}^{-1}$ ; Cu 0.90–4.02  $\mu\text{g g}^{-1}$ ), while muscle always exhibited the lowest levels (Hg 1.03–2.58  $\mu\text{g g}^{-1}$ ; Cd 0.01–0.06  $\mu\text{g g}^{-1}$ ;

Pb 0.02–0.16  $\mu\text{g g}^{-1}$ ; Cr 0.05–0.28  $\mu\text{g g}^{-1}$ ; Ni 1.13–2.48  $\mu\text{g g}^{-1}$ ; Zn 2.64–5.06  $\mu\text{g g}^{-1}$ ; Cu 0.33–2.23  $\mu\text{g g}^{-1}$ ). Ni and Hg took exception having the highest concentrations in brain and muscle, respectively. An assessment of the risk for human due to the consumption of these marine organisms was also undertaken. Regarding Cd and Pb intakes, consumption did not guide to any concerns, while it should be extremely moderate when considering Hg intake. The comparative analyses revealed that Mediterranean sharks were exposed to higher Hg levels than biota inhabiting open ocean.

**Keywords** Mediterranean Sea · Metals · Shark · Tissue distribution · PTWI

## Introduction

Trace metals are considered as serious pollutants of the aquatic environment because of their toxicity, high persistence, difficult biodegradability, and tendency to bioaccumulate in organisms. Sharks are top predators and are believed to play a significant role in aquatic food webs (Bowen 1997). The mean trophic levels of sharks (Cortès 1999) are similar to those described for marine mammals (Pauly et al. 1998) and are somewhat higher than those of seabirds (Hobson et al. 1994), whether estimated using dietary analyses or stable isotopes. As for marine mammals and seabirds,

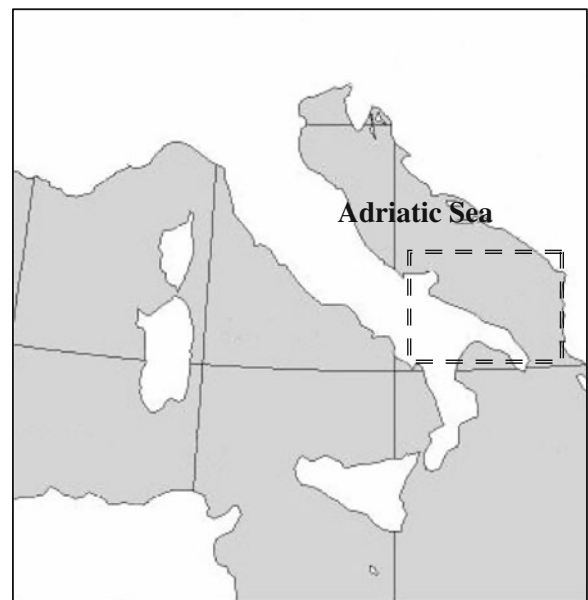
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sharks are particularly susceptible of accumulating significant levels of trace metals in their tissues, resulting key indicators of the environmental contamination status (Marcovecchio et al. 1991; Vas 1991). Previous studies have, in fact, demonstrated the ability of elasmobranch fish to accumulate high concentrations of potentially toxic elements, such as mercury and methylmercury (Pethybridge et al. 2010; Storelli et al. 2001, 2002), arsenic (Storelli and Marcotrigiano 2004; Storelli et al. 2005; Windom et al. 1973), as well as copper and zinc (Lowman et al. 1966). This aspect is especially interesting for biota residing in contaminated marine areas. It has been often reported that the Mediterranean Sea is at high toxicological risk (Meadows 1992; Kuetting 1994), as a consequence of its particular hydrographical characteristics and high pressure of the human impact. The Adriatic Sea, in particular, is a shallow and semi-enclosed basin which receives some of the largest Italian rivers, such as Po, Adige, and Brenta. This, in combination with contaminant inputs originating directly from industrial and urban sources located along the coast, makes this environment particularly interesting from the point view of contamination. Nevertheless, trace metal concentrations in these organisms are not well documented either in the Mediterranean area or in other marine regions, and the few studies concentrate on muscle tissue and/or liver only (Adams and McMichael 1999; Endo et al. 2008; Ferreira et al. 2004; Gibbs and Miskiewicz 1995; Lacerda et al. 2000; Mársico et al. 2007; McMeans et al. 2007; Pinho et al. 2002; Powell and Powell 2001; Serrano et al. 1997, 2000; Storelli and Marcotrigiano 2002; Storelli et al. 2003; Turoczy et al. 2000), without any broader picture of the accumulation processes and distribution of the metals among the other tissues. According to the mechanisms of absorption, regulation, storage, and excretion of metals, the various fish tissues present varying bioaccumulation rates and due to their different roles in the above processes, their analysis lead to results with special interest and interpretation (Catsiki and Stroglyoudi 1999). In addition, increased landings of sharks for human consumption in European waters (Biessi 1994) has prompted the need for more detailed information regarding either essen-

tial metals known to perform important functions in the biological systems or toxic metals which can be very harmful because of potential effects on fish themselves and people that consume them. With this background, this study reports the concentrations of trace elements (Hg, Cd, Pb, Cr, Ni, Cu, and Zn) in different tissues (muscle tissue, gonads, skin, and brain) of smooth hound *Mustelus mustelus* from the Mediterranean Sea (Adriatic Sea), common species in this water body and of high commercial importance. The main objectives of this work were: (a) to provide a picture of the partitioning of metals among the selected tissues; (b) to compare metal levels with those in other shark specimens living elsewhere in order to assess indirectly the pollution level of the Mediterranean marine environment; (c) to control the metallic content of fish for public health purposes.

## Materials and methods

During the period June–August 2009, specimens of smooth hound *M. mustelus* (no. of specimens, 22), all females, were caught by trawls in the South Adriatic Sea (Fig. 1). The Southern Adriatic surface waters are characterized by the



**Fig. 1** Sampling area

**Table 1** Method performance for determination of trace elements: accuracy, limits of detection (LOD), and limits of quantification (LOQ)

Element	TORT-2 ( $\mu\text{g g}^{-1}$ dry weight) <sup>a</sup>			LOD <sup>b</sup> ( $\text{ng g}^{-1}$ wet weight)	LOQ
	Certified	Measured	Recovery (%)		
Hg	0.27 ± 0.06	0.28 ± 0.03	104	5	13
Cd	26.7 ± 0.60	26.2 ± 2.4	98	0.10	0.38
Pb	0.35 ± 0.13	0.32 ± 0.18	91	10	40
Cr	0.77 ± 0.15	0.73 ± 0.16	95	5	16
Cu	106 ± 10	101 ± 13	95	25	80
Zn	180 ± 6	188 ± 12	104	25	85
Ni	2.50 ± 0.19	2.55 ± 0.21	102	25	80

<sup>a</sup>*n* = 3

<sup>b</sup>LOD = 3\*standard deviation of the blank

following chemical parameters: temperature, 16°C; salinity, 38.5 PSU; dissolved oxygen 5.42 ml l<sup>-1</sup> (Zavatarelli et al. 1998; Giordani et al. 2002). Adequate information on the age of this species in the Mediterranean Sea is lacking. However, on the basis of the data reported by Goosen and Smale (1997), the age of these specimens is approximately from 15 to 17 years. From each specimen, muscle tissue, gonads, skin, and brain were taken and kept in a deep freeze at -20°C until chemical analysis. The extractive analytical procedure and the instrumental conditions to determine metal concentrations have been described in detail elsewhere (Storelli et al. 2003; Storelli 2008). Briefly, aliquots (about 1.5–2.5 g) of the homogenized samples were digested to a transparent solution with a mixture of HNO<sub>3</sub>–HClO<sub>4</sub> (8:3) for Cd, Pb, Cr, Ni, Zn, and Cu determination and with a mixture of H<sub>2</sub>SO<sub>4</sub>–HNO<sub>3</sub> (1:1) for Hg. The completely digested samples were allowed to cool at room temperature and diluted with deionized water. The metal content was determined by atomic absorption spectroscopy (AAS; Perkin Elmer Analyst 800). Zn was analyzed by flame AAS, Cd, Pb, Cr, Ni, and Cu by graphite furnace technique (THGA-800 P.E.) and Hg by a hydride system (FIMS100) after reduction by SnCl<sub>2</sub>. Accuracy of these analyses was checked using a standard reference material from National Research Council of Canada (TORT-2 Lobster Hepatopancreas; Table 1). Standard error from triplicate analysis was less than 6% for each element. Trace metal concentrations were determined on a wet weight basis.

### Statistical analyses

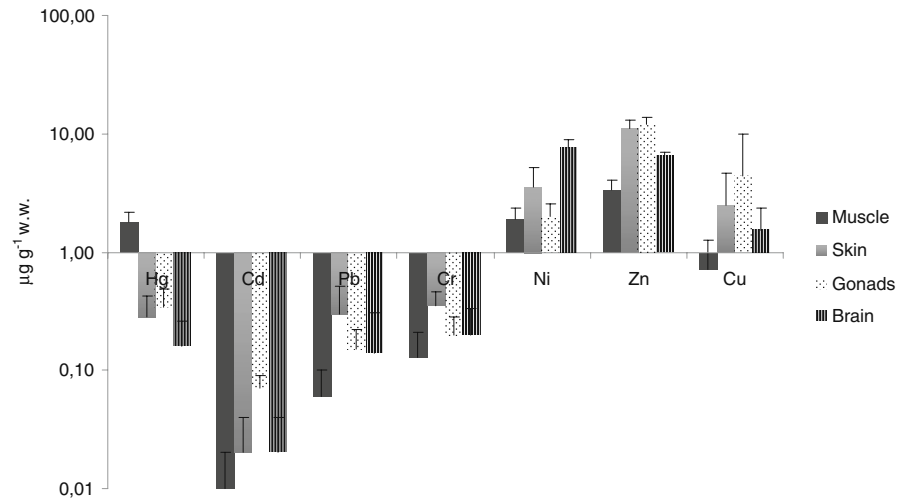
To test the differences between the concentrations in tissues of the samples, one-way ANOVA was performed. Post hoc test (Tukey) was applied to determine statistically significant differences following ANOVA. Some data had to be log transformed in order to fit ANOVA assumptions. Possibilities less than 0.05 were considered statistically significant (*p* < 0.05)

## Results and discussion

### Tissue/organ distribution of concentrations

Mean values for trace metals measured in the four tissues of smooth hound are illustrated in Fig. 2. Zn had the highest concentrations followed by Ni, Cu, Cr, Hg, Pb, and Cd. The data also revealed that metals were differentially distributed in the various part of the fish body. The highest Hg concentrations were found in muscle (1.77  $\mu\text{g g}^{-1}$ ), with levels many times higher (*p* < 0.05) than the other tissues which showed a content of similar magnitude. Cd accumulation did not vary in the examined tissues, except for gonads that showed a higher accumulation (0.07  $\mu\text{g g}^{-1}$ ; *p* < 0.05). The concentrations of Pb in skin (0.30  $\mu\text{g g}^{-1}$ ) were twice as high as in gonads (0.15  $\mu\text{g g}^{-1}$ ) and brain (0.14  $\mu\text{g g}^{-1}$ ; *p* < 0.05), whereas the lowest levels were found in muscle tissue (0.06  $\mu\text{g g}^{-1}$ ). Cr made up the highest concentrations in skin (0.35  $\mu\text{g g}^{-1}$ ; *p* < 0.05) and the lowest in muscle tissue (0.13  $\mu\text{g g}^{-1}$ ),

**Fig. 2** Mean concentrations ( $\pm$ SD) of metals in different tissues of smooth hound *M. mustelus*



while gonads and brain showed intermediate levels and equal between them ( $0.20 \mu\text{g g}^{-1}$ ). For Ni, the concentrations in muscle tissue ( $1.88 \mu\text{g g}^{-1}$ ) and gonads ( $2.01 \mu\text{g g}^{-1}$ ) were of similar magnitude and a few times lower than in skin ( $3.55 \mu\text{g g}^{-1}$ ), while the highest levels were found in brain ( $7.59 \mu\text{g g}^{-1}$ ). Cu content in gonads ( $4.39 \mu\text{g g}^{-1}$ ) was higher than those observed in skin ( $2.49 \mu\text{g g}^{-1}$ ) and in other tissues (brain  $1.53 \mu\text{g g}^{-1}$ ; muscle  $0.71 \mu\text{g g}^{-1}$ ;  $p < 0.05$ ), while for Zn, the highest concentrations were in gonads ( $12.00 \mu\text{g g}^{-1}$ ) and skin ( $11.00 \mu\text{g g}^{-1}$ ;  $p < 0.05$ ), followed by brain ( $6.49 \mu\text{g g}^{-1}$ ) and muscle tissue ( $3.38 \mu\text{g g}^{-1}$ ). Generally, the present data showed that concentrations of both essential and nonessential metals were higher in gonads and skin than brain, while muscle always exhibited the lowest concentrations. Ni and Hg were the only exceptions having the highest concentrations in brain and muscle, respectively. Differences in tissue metabolism play an important role in metal accumulation. It is clear that metabolically active tissues such as liver, kidney, and in our case gonads have a tendency to accumulate metals in higher values as observed in experimental (Kalay and Erdem 1995) and field studies (Karadede and Unlu 2000; Unlu et al. 1996). However, concentrations of trace metals can vary in different degrees depending on the considered tissues also as result of the different biochemical characteristics of the tissues. The relative amount of reactive groups and their availability for the syn-

thesis of metal-organic complexes specific for every organ can, for example, influence trace metal accumulation. In our case, the synthesis of particular low-molecular proteins with mercaptan groups (metallothioneins) in gonads could explain the enrichment of some elements, such as Cd, Zn, and Cu in these organs. In the same way, the low concentrations of the above mentioned metals in fish muscle may reflect the low levels of such binding proteins. Also, the higher bioaccumulation potential displayed by skin for a range of trace metals could be related to its chemical composition. The main placoid scale components, such as collagen, glycosaminoglycans, and apatite, are all substances that are suggested or known to display high affinity for metal ions (Passow 2002). Jeffrey et al. (2006) suggested that particular sorptive qualities of collagen, principal components of the shark dermis, may be responsible for the high metal concentrations, particularly pronounced for Zn. Concerning Ni, the examination of the order of accumulation emphasized the importance of this metal to brain. This relevance is difficult to explain, especially due to the lack of experimental studies on elamobranch fish. It might be supposed that olfactory neurons provide an important route by which Ni taken up in the olfactory epithelium may be transported to brain as observed in pikes (*Esox lucius*; Tallkvist et al. 1998). However, Pane et al. (2003) in rainbow trout exposed to waterborne Ni found that this metal is not significantly accumulated by brain. Further studies will be

needed to address this question. In the case of Hg, uptake and bioconcentration of this metal by marine organisms is a very efficient process. This is largely due to the high permeability through biological membranes of certain neutral complexes (Mason and Jenkins 1995), and its high affinity for proteinaceous material, which retains the molecule within the muscle tissue. It is known, in fact, that from 60% to 90% of its absolute content resides in muscles for different fish species (Harris et al. 2003; Kovekovdova and Simokon 2002).

#### Comparison with published data

Table 2 shows a comparison of our results with those of other researchers who have taken into consideration metal concentrations in elasmobranch fish from different marine areas. It is evident that information regarding tissue distribution of metals in sharks is fragmented, except for Hg presence in muscular tissue. Hg levels quite always high have, in fact, been reported in the muscle of various shark species from marine worldwide (Storelli et al. 2001, 2002, 2003, 2005; Adams and McMichael 1999; Ferreira et al. 2004; Pinho et al. 2002; Turoczy et al. 2000; Pethybridge et al. 2010). The biological traits of these animals as longevity and slow growth rates, in conjunction with the high trophic status of many shark species, have been invoked to explain the high levels encountered in their meats (Lyle 1984). Concerning shark gonads, there are no published Hg values for comparison, while the few literature data (Núñez-Nogueira 2005; Pethybridge et al. 2010; Windom et al. 1973) revealed higher brain levels and comparable skin levels ( $0.02\text{--}0.28\ \mu\text{g g}^{-1}$ ; Pethybridge et al. 2010) with respect to those encountered in the organisms under study. Higher Cd levels were found in brain (Núñez-Nogueira 2005) and skin (Vas 1991) of specimens from Atlantic Ocean, whereas good agreement was generally observed when muscle tissue results were compared with those reported in literature by several authors (Cornish et al. 2007; Hornung et al. 1993; Lacerda et al. 2000; Powell and Powell 2001; Turoczy et al. 2000). Also, Pb concentrations occurring in muscle tissue (Gibbs and Miskiewicz 1995; Storelli et al. 2003; Turoczy et al. 2000; Vas 1991), skin, and gonads (Vas 1991) of the speci-

mens here examined were within the previously reported ranges for other shark species, but the levels in brain were many times lower than the values displayed in literature (Núñez-Nogueira 2005). Nonessential metals do not present any function for the fish's metabolism and are by consequent not regulated by the organism. The amount of Hg, Cd, and Pb in fish can, thus, serve as an indication of environmental levels of these metals. In our study, although not always in significant proportions, Hg mean levels in muscle tissue of Mediterranean sharks were higher than those in elasmobranch from other international waters. This difference may be explained by shifts in the species' dietary prey composition and/or trophic position as well as differences in environmental levels. To this latter regard, it has been many times postulated that Hg enrichment in Mediterranean fish might be due not only to anthropogenic sources but also to natural Hg deposits and/or particular physicochemical conditions of waters of this semi-enclosed basin as high temperatures and absence of solar radiation in the deep waters. These conditions determine a higher net methylation rate in the deep environment and consequently a mayor bioavailable of methyl Hg for marine biota (Bacci 1989). As for the other metals discussed above, no study has quantified Cr concentrations in gonads and skin of any shark species, and so, no comparison is possible. For muscle, instead, Cr levels were more or less within the same order of magnitude as those reported in the same tissue of other shark species (Cornish et al. 2007; Gibbs and Miskiewicz 1995; Storelli et al. 2003), while for brain, literature data (Núñez-Nogueira 2005) were slightly higher than those here reported. Regarding essential metals Cu and Zn, published data ranged widely depending on the species. It has been suggested that such variance could be attributed either to different physiological requirements by the different shark species or the fact that metabolic regulation of essential elements may not be highly efficient in these cold-blooded fishes (McMeans et al. 2007). Relatively to Ni, the levels encountered in skin were similar to those reported for various shark species by Vas (1991), while concentrations in gonads and muscle tissue partially agreed with literature data (Vas 1991; Vas and Gordon 1993)

**Table 2** Summary of existing data on metal concentrations ( $\mu\text{g g}^{-1}$  w/w) in muscle, gonads, skin, and brain tissues of different shark species

Species	Hg	Cd	Pb	Cr	Ni	Zn	Cu	Provenience	Reference
<b>Muscle</b>									
<i>Mustelus mustelus</i>	1.77	0.01	0.06	0.13	1.88	3.38	0.71	Mediterranean Sea	Present study
<i>Sphyrna zygaena</i>	12.15	0.03	0.02	0.18	–	6.97	1.45	Mediterranean Sea	Storelli et al. (2003)
<i>Centrophorus granulosus</i>	0.48–8.37	0.06	–	–	–	3.13	0.36	Mediterranean Sea	Hornung et al. (1993)
<i>Etmopterus spinax</i>	1.83–4.58	0.08	–	–	–	4.93	0.58	Mediterranean Sea	Hornung et al. (1993)
<i>Galeus melastomus</i>	0.99–8.76	0.07	–	–	–	3.63	0.45	Mediterranean Sea	Hornung et al. (1993)
<i>Hexanchus griseus</i>	–	0.04	–	–	–	4.28	0.31	Mediterranean Sea	Hornung et al. (1993)
<i>Somniosus rostratus</i>	–	0.07	–	–	–	4.53	0.64	Mediterranean Sea	Hornung et al. (1993)
<i>Prionace glauca</i>	–	0.45	<0.02	–	2.58	–	0.24	Atlantic Ocean	Vas (1991)
<i>Scyliorhinus canicula</i>	–	1.08	0.35	–	<0.02	–	2.42	Atlantic Ocean	Vas (1991)
<i>Galeorhinus galeus</i>	–	<0.02	0.16	–	1.79	2.12	0.44	Atlantic Ocean	Vas (1991)
<i>Lamna nasus</i>	–	0.79	–	–	–	7.21	–	Atlantic Ocean	Vas (1991)
<i>Scyliorhinus canicula</i>	–	0.78	1.88	–	1.70	–	0.39	Atlantic Ocean	Vas (1991)
<i>Scyliorhinus stellaris</i>	–	<0.02	<0.02	–	<0.02	–	0.56	Atlantic Ocean	Vas (1991)
<i>Scymnorhinus licha</i>	–	<0.02	<0.05	–	–	<0.05	–	Atlantic Ocean	Vas (1991)
<i>Etmopterus spinax</i>	–	0.25	<0.10	–	–	<0.05	–	Atlantic Ocean	Vas (1991)
<i>Galeus melastomus</i>	–	0.08	0.16	–	1.41	–	0.22	Atlantic Ocean	Vas (1991)
<i>Apristurus spp.</i>	–	–	–	–	0.36	–	0.41	Atlantic Ocean	Vas and Gordon (1993)
<i>Centroscyllium fabricii</i>	–	–	–	–	0.43	–	0.07	Atlantic Ocean	Vas and Gordon (1993)
<i>Centroscymnus coelepis</i>	–	–	–	–	0.98	–	0.19	Atlantic Ocean	Vas and Gordon (1993)
<i>Centroscymnus crepidator</i>	–	–	–	–	<0.02	–	1.91	Atlantic Ocean	Vas and Gordon (1993)
<i>Dalatias licha</i>	–	–	–	–	<0.02	–	3.80	Atlantic Ocean	Vas and Gordon (1993)
<i>Deania calcea</i>	–	–	–	–	2.77	–	<0.02	Atlantic Ocean	Vas and Gordon (1993)
<i>Etmopterus princeps</i>	–	–	–	–	0.37	–	0.13	Atlantic Ocean	Vas and Gordon (1993)
<i>Etmopterus spinax</i>	–	–	–	–	1.54	–	5.31	Atlantic Ocean	Vas and Gordon (1993)
<i>Galeus murinus</i>	–	–	–	–	<0.02	–	<0.02	Atlantic Ocean	Vas and Gordon (1993)
<i>Carcharhinus limbatus</i>	3.33	0.35	2.51	0.44	–	43.97	1.06	Atlantic Ocean	Núñez-Nogueira (2005)
<i>Rhizoprionodon terraenovae</i>	0.76	0.34	3.31	0.45	–	11.91	1.10	Atlantic Ocean	Núñez-Nogueira (2005)
<i>Centroscymnus crepidator</i>	1.08	–	<0.03	–	<0.01	2.20	0.07	Pacific Ocean	Turoczy et al. (2000)
<i>Centroscymnus owstonii</i>	2.98	0.01	<0.03	–	<0.01	2.40	0.01	Pacific Ocean	Turoczy et al. (2000)
<i>Deania calcea</i>	1.80	0.01	<0.03	–	<0.1	2.00	0.06	Pacific Ocean	Turoczy et al. (2000)
<i>Carcharhinus limbatus</i>	0.24	0.01	0.16	–	–	3.11	0.31	Pacific Ocean	Powell and Powell (2001)
<i>Rhizoprionodon acutus</i>	0.10	0.01	0.16	–	–	3.13	0.29	Pacific Ocean	Powell and Powell (2001)



<i>Sphyrna lewini</i>	0.38	0.02	0.14	–	–	3.80	0.37	Pacific Ocean	Powell and Powell (2001)
<i>Heterodontus portusjacksoni</i>	1.64	0.01	0.01	0.14	–	5.52	0.22	Pacific Ocean	Gibbs and Miskiewicz (1995)
<i>Isurus oxyrinchus</i>	1.58	–	–	–	–	4.00	0.35	Pacific Ocean	Vlieg et al. (1993)
<i>Lamna nasus</i>	0.68	–	–	–	–	4.00	0.40	Pacific Ocean	Vlieg et al. (1993)
<i>Carcharhinus albimarginatus</i>	1.80	–	–	–	–	3.40	–	Pacific Ocean	Endo et al. (2008)
<i>Carcharhinus plumbeus</i>	1.66	–	–	–	–	3.35	–	Pacific Ocean	Endo et al. (2008)
<i>Carcharhinus leucas</i>	3.65	–	–	–	–	4.36	–	Pacific Ocean	Endo et al. (2008)
<i>Galeocerdo cuvier</i>	0.78	–	–	–	–	4.72	–	Pacific Ocean	Endo et al. (2008)
<i>Chiloscyllium plagiosum</i>	–	0.01	<0.001	0.21	<0.001	7.42	0.15	Pacific Ocean	Cornish et al. (2007)
<b>Gonads</b>									
<i>Mustelus mustelus</i>	0.34	0.07	0.15	0.20	2.01	12.00	4.39	Mediterranean Sea	Present study
<i>Etmopterus spinax</i>	–	<0.02	<0.10	–	–	1.53	–	Atlantic Ocean	Vas (1991)
<i>Galeorhinus galeus</i>	–	<0.02	0.69	–	8.30	–	0.10	Atlantic Ocean	Vas (1991)
<i>Galeus melastomus</i>	–	0.06	0.02	–	1.69	–	0.11	Atlantic Ocean	Vas (1991)
<i>Scyliorhinus canicula</i>	–	<0.02	<0.02	–	0.50	–	0.95	Atlantic Ocean	Vas (1991)
<i>Scyliorhinus canicula</i>	–	0.95	<0.02	–	<0.02	–	2.22	Atlantic Ocean	Vas (1991)
<i>Scyliorhinus stellaris</i>	–	<0.02	–	–	–	–	4.88	Atlantic Ocean	Vas (1991)
<b>Skin</b>									
<i>Mustelus mustelus</i>	0.28	0.02	0.30	0.35	3.55	11.00	2.49	Mediterranean Sea	Present study
<i>Scymnorhinus licha</i>	–	0.48	<0.05	–	–	4.04	–	Atlantic Ocean	Vas (1991)
<i>Etmopterus spinax</i>	–	0.38	0.43	–	–	17.86	–	Atlantic Ocean	Vas (1991)
<i>Galeorhinus galeus</i>	–	<0.02	0.34	–	3.42	4.23	1.83	Atlantic Ocean	Vas (1991)
<i>Galeus melastomus</i>	–	0.08	<0.02	–	2.01	–	0.57	Atlantic Ocean	Vas (1991)
<i>Prionace glauca</i>	–	0.97	3.63	–	1.00	–	0.26	Atlantic Ocean	Vas (1991)
<i>Scyliorhinus canicula</i>	–	0.95	<0.02	–	1.29	–	12.10	Atlantic Ocean	Vas (1991)
<i>Scyliorhinus canicula</i>	–	1.07	<0.02	–	<0.02	–	4.84	Atlantic Ocean	Vas (1991)
<i>Scyliorhinus stellaris</i>	–	<0.02	<0.02	–	2.30	–	1.17	Atlantic Ocean	Vas (1991)
<b>Brain</b>									
<i>Mustelus mustelus</i>	0.16	0.02	0.14	0.20	7.59	6.49	1.53	Mediterranean Sea	Present study
<i>Carcharhinus falciformi</i>	2.00	<0.20	–	–	–	10.00	8.40	Atlantic Ocean	Windom et al. (1973)
<i>Carcharhinus limbatus</i>	1.33	1.33	2.92	0.56	–	24.42	6.95	Atlantic Ocean	Núñez-Nogueira (2005)
<i>Carcharhinus obscurus</i>	2.90	<0.10	–	–	–	27.00	8.40	Atlantic Ocean	Windom et al. (1973)
<i>Rhizoprionodon terraenovae</i>	0.45	2.14	7.91	1.10	–	31.37	6.63	Atlantic Ocean	Núñez-Nogueira (2005)

which showed a high interspecies variability. Such a variation is, however, unsurprising because it has been already said that concentration of Ni in fish is directly related to the level of contamination in the water (Kashulin and Reshetnikov 1995).

### Fish quality for human consumption

In relation to impact of metals on human health, the muscle tissue of fish has been investigated more than other organs because it is the fish part usually consumed by human. Concentrations of Cd and Pb as reported in this study did not constitute a risk factor for human health being below the permissible limits for human consumption set by the European Union which are 0.05 and 0.30  $\mu\text{g g}^{-1}$  wet weight (Official Journal of the European Communities 2006, 2008), respectively. Conversely, Hg concentrations exceeded the proposed limit value which is 1.0  $\mu\text{g g}^{-1}$  wet weight (Official Journal of the European Communities 2008), confirming once a time that the consumption of certain fish can pose a potential threat to the health of consumer. For the remaining metals, legal thresholds are inexistent in Europe. Consequently, an evaluation of the chemical quality of these fish is possible only utilizing guidance values fixed in other countries. Comparison with the Turkish standards (Cu 20  $\mu\text{g g}^{-1}$ ; Zn 50  $\mu\text{g g}^{-1}$ ; 2002) and Western Australian accepted limits (Cr and Ni 5.5  $\mu\text{g g}^{-1}$ ; Zn 40  $\mu\text{g g}^{-1}$ ; Cu 10  $\mu\text{g g}^{-1}$ ; Turan et al. 2009; Usero et al. 2003) demonstrated that the content of these metals in the edible part of the examined fish was lower than the guidelines mentioned above. However, when considering the chemical quality of fish destined for food consumption, it is worth asking whether the metals present in their meats can have a negative impact on consumer's health. According to the Joint Food and Agriculture Organization/World Health Organization (WHO 2003; EFSA 2009) the provisional tolerable weekly intakes (PTWI) for Hg, Cd, and Pb are 5, 2.5, and 25  $\mu\text{g kg}^{-1}$  body weight, respectively. On the basis of a weekly average consumption of fishery products in Italy of 462 g (FAO 2008), an average human body weight of 60 kg and the average Hg, Cd, and Pb values found in this study, the estimated weekly intakes of Cd (0.08  $\mu\text{g kg}^{-1}$  body weight) and Pb (0.04  $\mu\text{g kg}^{-1}$

body weight) were much lower than the established safety values, while PTWI of 5  $\mu\text{g kg}^{-1}$  body weight for Hg was largely exceeded when this species was consumed (13.63  $\mu\text{g kg}^{-1}$  body weight). However, the values of Hg might be overestimated because it would be very unlikely for a person to consume the aforementioned amount of this species per week. It should be, anyway, emphasized that a weekly consumption equal to half (231 g) of those on average esteemed in Italy determined an intake (6.81  $\mu\text{g kg}^{-1}$  body weight) exceeding the WHO safety limit, making regular shark dietary consumption a significant risk factor for human.

### Conclusion

The present work provides new information on the distribution of trace elements in different tissues of sharks from the Mediterranean Sea. The results obtained show that the element concentrations vary substantially according to the tissue or organ taken into consideration. Hg, particularly concentrated in the muscle tissue of this commercially important shark species, is a problem which deserves attention, above all in relation to increased landings of sharks for human consumption. The muscle Hg values are, in fact, alarming if referring either to the total Hg contamination level limit for fish products destined for food consumption or the maximum permissible dietary intake concentration established by WHO. Our data also reveal that Mediterranean sharks are exposed to higher levels of Hg than biota inhabiting open ocean. This elevation may result from a combination of factors including either natural geochemical processes or anthropogenic sources. Very little element data exist for sharks, and there is a need to better understand the assimilation, distribution, and elimination of both nonessential and essential elements, which may contribute to explain the mechanisms by which pollution of the marine environment affects the species living in it and human health.

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