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Levels of Total Mercury in Marine Organisms from Adriatic Sea, Italy

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Abstract The presence of total mercury in fish, crustacean and cephalopod from Adriatic Sea, was investigated. The highest concentrations were observed in decreasing order in: Norway lobster (0.97 ± 0.24 mg/kg; mean ± SE), European hake (0.59 ± 0.14 mg/kg), red mullet (0.48 ± 0.09 mg/kg), blue whiting (0.38 ± 0.09 mg/kg), Atlantic mackerel (0.36 ± 0.08 mg/kg) and European flying squid (0.25 ± 0.03 mg/kg). A significant difference ($p < 0.01$) was found between the levels of total mercury in Norway lobster and those detected in all other species. The 25% of all samples exceeded the maximum limit fixed by Commission Regulation (EC) No 1881/2006. The results show that fish and fishery products can exceed the maximum levels and stress the need of more information for consumers in particular for people that eat large amount of fish.

Keywords Total mercury · Fish · Cephalopod · Crustacean

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Mercury (Hg) is broadly spread in the environment, occurring, at different concentrations, in air, bedrock, soil, water and all biological matters. It presents itself in two distinct forms: the metallic or inorganic mercury and the organic mercury. Urbanization and anthropogenic activities have contributed to elevate levels of mercury in the atmosphere and the related atmospheric deposition is often the main source of Hg to the aquatic system.

The toxicity of mercury derives from its extreme volatility, its relative solubility in water and lipids, and its capacity to bind with other molecules. In the aquatic ecosystem mercury tends to be adsorbed by particles and deposited into sediments. There, under certain conditions, bacteria convert metallic or elemental forms of mercury to methylmercury (Ullrich et al. 2001). Dissolved organic matter in aquatic environments is known to bind trace metals strongly, affecting their speciation, solubility, mobility and toxicity. Methylmercury (MeHg) can be adsorbed in particles or from the water by small creatures such as shrimp and other invertebrates, which then are consumed by predators including fish. Among fish, benthic and predatory pelagic species accumulate this form of mercury. It must be noted that this accumulation occurs largerly through food chain transfer (biomagnification) and not through direct uptake from water or sediments. It is well known that MeHg is more toxic than inorganic mercury and is extremely toxic to marine organisms, wildlife and human. It affects the immune system, alters genetic and enzyme system and damages the nervous system (Hempel et al. 1995). In human the dietary intake is the main route of exposure to MeHg and fish represent the most common source all around the world.

Food and Drug Administration established a Tolerable Daily Intake (TDI) based on a weekly tolerance of 0.3 mg of total mercury per person, of which no more than 0.2 mg should be present as methylmercury. These amounts are equivalent to 5 and 3.3 µg, respectively, per kilogram of body weight (bw). Using the values for methylmercury, this tolerable level would correspond to approximately 230 µg/week for a 70 kg person or 33 µg/person/day (0.47 µg/kg bw/day). The maximum levels fixed by Commission Regulation (EC) No 1881/2006 of 19 December 2006 (Commission Regulation EC 2006), for total mercury is 0.50 mg/kg in fishery products and muscle meat of fish, with the exception of certain listed fish species, for which a limit of 1.0 mg/kg was established. The maximum level of 0.50 mg/kg applies also to crustaceans, excluding the brown meat of crab and excluding head and thorax meat of lobster and similar large crustaceans (*Nephropidae* and *Palinuridae*). As fish consumption is the primary source of mercury to humans, the main purpose of this paper was to investigate the presence of total mercury in benthic, demersal and pelagic fish, crustaceans and cephalopods fished in the Adriatic Sea.

Materials and Methods

Fish, crustaceans and cephalopods were caught in the Central Adriatic Sea, Italy, by local boats using deep-sea trawls. All samples ($n = 82$) were collected during the year 2004. The organisms selected were: Norway lobster (*Nephrops norvegicus*), red mullet (*Mullus barbatus*), European flying squid (*Todarodes sagittatus*), Atlantic mackerel (*Scomber scombrus*), blue whiting (*Micromesistius poutassou*) and European hake (*Merluccius merluccius*). They were selected because they are widely distributed in the Central Adriatic Sea and are therefore reflective of species meant for consumption. The samples, all of commercial size, were wrapped in aluminum foil, then immediately frozen and transported to the laboratory. All samples were carefully dissected using clean equipment to separate the edible portion, fillet for fish and muscle for crustaceans and, after homogenization, stored at −20°C.

For analyses of total mercury a wet digestion method was used. Homogenized samples, close to 1 g, were freeze dried and aliquots of 200 mg were mineralized using nitric acid (2 mL). The vessel was placed into the bomb, placed into the microwave oven and irradiated for 150 s at 400 W. The digestion solutions were then diluted with deionized water to a final volume of 25 mL.

The total mercury concentrations were measured in inductively coupled plasma-atomic emission spectrophotometry using a Perkin Elmer Optima 2100 DV instrument with axial configuration coupled with a CETAC U5000AT+ hydride generator. Specimens were run in batches that included a blank, initial calibration standards and standard reference materials (BCR 422: cod muscle). All values of reference materials were within certified limits given by the Community Bureau of Reference–BCR (Brussels). Detection limit for mercury was 0.0610 µg/kg. Analytical CV was calculated and was always below 10%.

Statistical data analysis was performed with SPSS 14.0.2 (SPSS Inc., Chicago, IL, USA). Normality of data, calculated on a fresh basis, was assessed by means of Kolmogorov–Smirnov test. They were not normally distributed, even after log and square root transformation; therefore only non parametric statistical tests were used. In particular the Kruskal–Wallis test for independent samples (exact test extension) was performed to detect significant differences among groups ($\alpha = 0.05$).

Results and Discussion

Mercury was found in all samples at different concentrations, ranging from a minimum of 0.02 mg/kg in European flying squid to a maximum of 3.27 mg/kg in Norway lobster. The highest total mercury mean concentrations (Fig. 1) were observed in decreasing order in: Norway lobster (0.97 ± 0.24 mg/kg; mean ± SE), European hake (0.59 ± 0.14 mg/kg), red mullet (0.48 ± 0.09 mg/kg), blue whiting (0.38 ± 0.09 mg/kg), Atlantic mackerel (0.36 ± 0.08 mg/kg) and European flying squid (0.25 ± 0.03 mg/kg). A significant difference ($p < 0.01$) was found between the levels of total Hg in Norway lobster and those detected in all other species. More than 25% of all samples exceeded the maximum limit fixed by European Regulation. The percentages of samples for each species that exceeded the limit of 0.50 mg/kg were reported in Table 1. Among samples, only red mullet belongs to the species with a maximum limit of 1 mg/kg. This species showed total Hg levels higher than this limit in 21.4% of samples. It must be underlined, however, that samples were collected from local boats as soon as they entered harbour and no official control was made by the competent authority to assess if mercury concentrations were under the legal limit.

The variability of total Hg concentrations in the analyzed species (Table 2) could be attributed to several factors: fish physiology, habitat, trophic level, age and body weight. Based on feeding habits, many studies showed that piscivores had higher Hg levels than herbivores and detritivores (Storelli and Marcotrigiano 2004). Also planktophagus fish species could present high total mercury levels, as a consequence that plankton plays an important role in the transfer of Hg from the atmospheric compartment into the aquatic ecosystem or from sediment into the aquatic food chain. By excluding Norway lobster, in this study the highest mean concentrations of total Hg were found in piscivores as a consequence of bioaccumulation

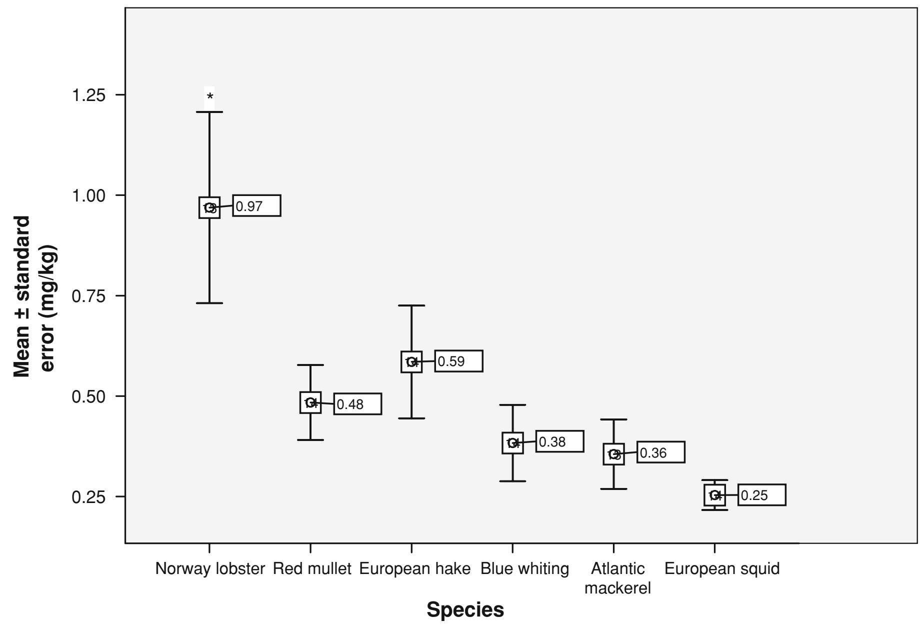

Fig. 1 Mean and standard error (mg/kg) of total mercury in the selected species

Table 1 Percentages of species exceeding the maximum levels for total mercury

Species	Habitat	Feeding habits	Over limits[a] (%)
Norway lobster	Benthonic	Detritivore	46.2
Red mullet	Demersal	Detritivore	21.4
European hake	Demersal	Piscivore	42.9
Blue whiting	Benthopelagic	Piscivore	14.3
Atlantic mackerel	Pelagic	Piscivore	23.1
European squid	Neritic	Piscivore	7.1
Total			25.6

[a] 0.50 mg/kg except for red mullet (1 mg/kg)

along the food chain, with European hake at the top of it. As reported by Stergiou and Karpouzi (2002), *M. merluccius* can be considered, together with *Conger conger*, *Thunnus thynnus* and *Xiphias gladius*, one of the top carnivores living in the Mediterranean Sea. Hg concentrations below 0.20 mg/kg have been usually observed in low trophic level fish species of small body weight (Peixoto Boischio and Henshel 2000). Forsberg et al. (1995) found average Hg concentrations in herbivore and omnivore species of 0.14 and 0.35 mg/kg, respectively. In our study the lowest Hg concentrations were found in European flying squid. Regarding to habitat, it has been reported that benthic fish show higher total mercury concentrations than pelagic fish (Storelli et al. 1998). Among the species selected in our study, only *N. norvegicus* is benthonic while the other species are demersal or pelagic. It can be assumed that Norway lobster showed the highest levels of total Hg because it is a scavenging animal that feeds on a wide range of decomposition residues, most constituting humic substances of the dissolved organic matter. It has been reported that this organic matter interacts very strongly with mercury and affects its bioavailability in aquatic environments (Ravichandran 2004). A large species-dependent variability was also observed by Storelli et al. (2003) in different fish species from the Adriatic Sea. In particular, they found mean total Hg concentrations ranging from a minimum of 0.08 µg/g in an herbivorous fish (*Sarpa salpa*, goldline) to a maximum of 0.76 µg/g in *Lophius budegassa*, angler fish.

Besides these interspecific differences among species, it must be underlined that mercury is unevenly distributed in the marine environment. The Mediterranean basin contains enormous cinnabar deposits and about 50%–55% of world mercury resources are located in the Mediterranean area. Renzoni et al. (1998) found high total mercury levels in Norway lobster coming from Tyrrhenian Sea, because this lives in deep water close to the upper layer of sediment, the site of mercury methylation. A positive correlation between mercury concentrations in sediment and mercury levels in benthic crustaceans and mollusks has been demonstrated in other parts of the Mediterranean (Hornung et al. 1984). A better understanding of mercury distribution in aquatic systems not only requires knowledge of total mercury, but also the amount of mercury that exists in methylated form which is much more available for bioaccumulation. Even if methylation process reflects biogeochemical adjustment within the sediment environment in response to mercury contamination, the mercury uptake by fish from waters with mercury contaminated sediments occurs readily because of the rapid transfer of MeHg from the sediments to the water column (Ikingura and Akagi 1999).

Table 2 Mean, standard error, minimum, maximum and range (mg/kg) of total mercury in analysed samples

Species	Mean	Standard error	Minimum	Maximum	Range	Number of samples
Lobster	0.97	0.24	0.29	3.27	2.98	13
Red mullet	0.48	0.09	0.05	1.07	1.02	14
European hake	0.59	0.14	0.04	1.99	1.95	14
Blue whiting	0.38	0.09	0.06	1.42	1.36	14
Atlantic mackerel	0.36	0.08	0.03	1.17	1.14	13
European squid	0.25	0.03	0.02	0.62	0.60	14

In view of recent reports regarding low-dose mercury toxicity (Knobeloch et al. 2006) its environmental contamination should be checked. In addition to the setting of maximum levels, targeted consumer advice is an appropriate approach in the case of methylmercury for protecting vulnerable groups of the population. People who eat large amounts of fish (even species with relatively low mercury content) can accumulate sufficient levels of MeHg to cause symptoms, and pregnant women can transfer to a foetus amounts of MeHg that are sufficient to impair nervous system development (Gochfeld 2003).

In 2003, the WHO lowered its provisional tolerable weekly intake (PTWI) for methylmercury to 1.6 µg/kg-bw, based on the most sensitive toxicological end-point (developmental neurotoxicity) in the most susceptible species (humans). It corresponds to a TDI of 0.23 µg/kg-bw. In the case of adults, the JECFA considered that intakes of up to about two times higher than the existing PTWI of 1.6 µg/kg-bw would not pose any risk of neurotoxicity in adults, although in the case of women of childbearing age, it should be borne in mind that intake should not exceed the PTWI, in order to protect the embryo and foetus (JECFA 2006). The results of this study showed that more than 25% of samples exceeded 0.5 mg/kg of total Hg. That means if humans, with an average body weight of 60 kg, consumed daily 32 g of fish (EFSA 2004) with a mean total mercury concentration of 0.50 mg/kg (calculated as the mean of all samples of this study), the average TDI is 0.27 µg/kg-bw. So, since the mercury content in fish is greater than 90% methylmercury, the average daily methylmercury intake is 0.24 µg/kg-bw. This estimated value exceeded the above mentioned TDI (0.23 µg/kg-bw) and it should be higher if considering populations with a high consumption of fishery products. As a consequence, fish advisories based on the difference in average Hg concentrations among species are needed. They should be addressed in particular to the vulnerable stages people in order to reduce Hg exposure. Foetuses and infants are in the most sensitive life stage with regard to health effects in association with maternal Hg exposure. Taking into account the important nutritional contribution that fish makes to the diet, the European Food Safety Authority (EFSA) recommends that women of childbearing age (in particular, those intending to become pregnant), pregnant and breastfeeding women as well as young children select fish from a wide range of species, without giving undue preference to large predatory fish such as swordfish and tuna. Due to their place in the food chain, these fish are likely to contain higher levels of methylmercury than other fish species. Since fish and fishery products frequently exceed the maximum levels fixed for total mercury, it would be prudent to continue systematic monitoring of the fish supply in order to avoid that contaminated foodstuffs will be placed on the market.

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