Ocean Sci. J. (2017) 52(4):527−536
http://dx.doi.org/10.1007/s12601-017-0044-1

Available online at http://link.springer.com
SpringerLink

pISSN 1738-5261
eISSN 2005-7172

Article

Concentrations of Heavy Metals in Marine Wild Fishes Captured from the Southern Sea of Korea and Associated Health Risk Assessments

Dong-Woon Hwang[1], Seong-Soo Kim[2], Seong-Gil Kim[2], Dong-Sun Kim[3], and Tae-Hoon Kim[4]*

[1]*Marine Environment Research Division, National Institute of Fisheries Science, Busan 46083, Korea*
[2]*Marine Environment Monitoring Team, Korea Marine Environment Management Corporation, Busan 49111, Korea*
[3]*Department of Ecological Engineering, College of Environmental and Marine Sciences and Technology, Pukyong National University, Busan 48513, Korea*
[4]*Department of Earth and Marine Sciences, College of Ocean Sciences, Jeju National University, Jeju 63243, Korea*

Received 10 January 2017; Revised 29 March 2017; Accepted 15 May 2017

Abstract – Concentrations of heavy metals (As, Cd, Cr, Cu, Hg, Pb, and Zn) were determined in edible parts (muscle) of 34 marine wild fish caught from the southern sea of Korea in 2007 and 2008 in order to understand the accumulation pattern of heavy metals in wild fish and to assess the potential health risk posed by fish consumption. The highest concentrations in the muscle of 17 pelagic and 17 demersal fishes were Zn and As, respectively, while the lowest concentration in both fishes was Cd. The mean concentrations of all metals except As in wild fish were much lower than the regulatory limits for fish and fishery products applied in a number of countries. Unlike other metals, As concentration in wild fish of this study region was relatively higher than that found in other country. Estimated daily intake (EDI) of the metals was in the range of 0.05% to 22.5% of the provisional maximum tolerable daily intakes (PMTDI). Similarly, the target hazard quotient (THQ) was below 1.0 for each metal. These results imply that the consumption of the investigated wild fish do not cause significant adverse health effects.

Keywords – wild fish, heavy metal, PMTDI, THQ, Korea

1. Introduction

Heavy metals are released artificially from anthropogenic sources through human and industrial activities as well as naturally from soil and rocks through weathering and erosion processes and continually enter into the ocean via atmospheric deposition, riverine input, and submarine groundwater discharge (Yuan et al. 2012; Li et al. 2013; Hwang et al. 2016). Heavy metals discharged into the marine environment can be accumulated in marine organisms through a number of pathways, including respiration, adsorption, and ingestion (Das et al. 2003; Terra et al. 2008; Kim et al. 2011; Zeng et al. 2012). Although heavy metals are necessary in a small amounts for the individual metabolic processes of marine organisms, some metals, such as Cd, Hg, and Pb, cause adverse effects in marine organisms and pose potential health risks to people who consume a contaminated seafood (Crump and Trudeau 2009; Qiu et al. 2011).

Fish, among marine organisms, contain high levels of protein, low saturated fat content, and omega-3 fatty acids, which are well known for their health benefits (Daviglus et al. 2002; Qiu et al. 2011). The protein derived from fish accounts for approximately 17% of the animal protein intake of the global human population and fish consumption is gradually increasing every year (FAO 2014). Especially, the fishery industry, including fish aquaculture, in coastal oceans has expanded rapidly around the world in the last few decades because of increasing demand for fish as a protein source (Belias and Dassenakis 2002; Dalsgaard and Kruse-Jensen 2006).

Korea is one of the countries with the highest per capita consumption rates of fish and fishery products in the whole world together with China, Japan, and Norway (Park et al. 2014; FAO 2016). The annual Korean per capita fish consumption rate gradually increased from 42.2 kg/year in 2001 to 54.9 kg/year in 2012 (KMOF 2014), and this has led to increasing concern about the safety of seafood including fish. The Korean

*Corresponding author. E-mail: thkim@jejunu.ac.kr

government has carried out an annual monitoring program in which the heavy metal concentrations of imported and domestic (farmed and wild) fish purchased from seafood markets are determined in order to protect the health of people consuming seafood (Kim et al. 2007; Mok et al. 2014). Nevertheless, little information is available on the accumulation of heavy metals in marine wild fish caught in Korean coastal waters.

In this study, we determined the concentrations of the heavy metals (As, Cd, Cr, Cu, Hg, Pb, and Zn) in the muscle of wild fish and assessed the potential health risks posed to people consuming marine fish. Here, we collected wild fish caught from the southern sea of Korea because more edible fishes inhabit and are caught in that sea than in the other seas (the Yellow Sea and the East Sea) around the Korean Peninsula (NFRDI 2014).

2. Materials and Methods

Sample collection

34 marine wild fish species (about 160 individuals) were collected from the largest fish market (Busan Cooperative Fish Market) in Korea and from a survey of fishery resources in the southern sea of Korea exclusive economic zone conducted by the National Fisheries Research and Development Institute in 2007 and 2008. After collection, 63 samples were obtained from one to sixteen individuals of each species. 32 samples were pelagic species (17 of fish species), and 31 samples were demersal species (17 of fish species) (Table 1). Each sample was placed in a vinyl zipper bag, immediately frozen, and stored at -20°C until analysis.

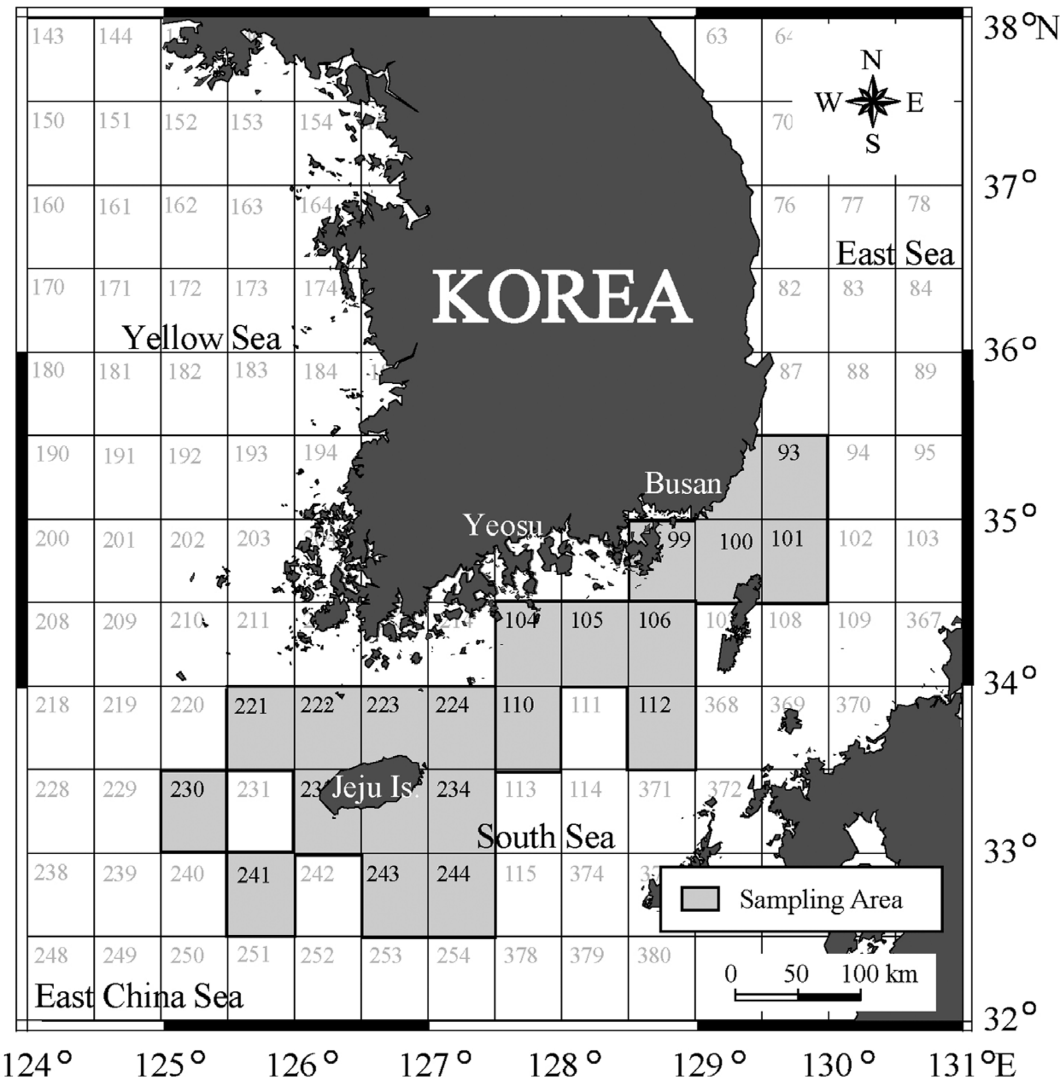

Fig. 1. A map showing the sampling area of 34 marine wild fish captured from the southern sea of Korea in 2007 and 2008

Table 1. The mean concentrations and standard deviation (SD) of heavy metals in muscle tissue of wild fish caught from the southern sea of Korea in 2007 and 2008. Different letters in mean ± SD lines indicate statistically significant differences ($p < 0.05$) between heavy metal concentrations in muscle of pelagic and demersal fishes. (ND = Not determined)

Species Common name	Scientific name		Concentration (µg/g-wet weight) As	Cd	Cr	Cu	Hg	Pb	Zn
Pelagic fish									
Bluefin tuna	*Thunnus thynnus*	(n = 2)	0.79 ± 0.52	0.004 ± 0.000	0.13 ± 0.03	0.45 ± 0.17	0.13 ± 0.05	0.13 ± 0.05	3.52 ± 2.40
Black scraper	*Thamnaconus modestus*	(n = 2)	4.41 ± 2.02	0.014 ± 0.019	0.10 ± 0.07	0.12 ± 0.01	0.01 ± 0.00	0.34 ± 0.44	3.56 ± 0.92
Chub mackerel	*Scomber japonicus*	(n = 1)	2.87	0.013	0.28	1.02	0.06	0.26	4.01
Dark-banded rockfish	*Sebastes inermis*	(n = 2)	3.03 ± 2.86	0.003 ± 0.001	0.11 ± 0.01	0.21 ± 0.17	0.05 ± 0.02	0.02 ± 0.00	4.54 ± 1.79
Flathead mullet	*Mugil cephalus cephalus*	(n = 2)	0.91 ± 0.30	0.001 ± 0.002	0.10 ± 0.01	0.49 ± 0.22	0.01 ± 0.01	0.01 ± 0.00	2.95 ± 0.27
Japanese amberjack	*Seriola quinqueradiata*	(n = 2)	1.79 ± 1.27	0.075 ± 0.102	0.15 ± 0.01	0.87 ± 0.09	0.08 ± 0.01	0.15 ± 0.08	5.10 ± 0.84
Japanese anchovy	*Engraulis japonicus*	(n = 3)	2.75 ± 2.09	0.008 ± 0.010	0.12 ± 0.03	1.83 ± 0.25	0.05 ± 0.03	0.01 ± 0.01	13.28 ± 3.51
Japanese jack mackerel	*Trachurus japonicus*	(n = 2)	4.20 ± 2.18	0.001 ± 0.000	0.11 ± 0.00	0.33 ± 0.21	0.05 ± 0.02	0.01 ± 0.01	3.41 ± 0.15
Japanese seaperch	*Lateolabrax japonicus*	(n = 2)	3.15 ± 4.18	0.003 ± 0.001	0.11 ± 0.07	0.16 ± 0.00	0.09 ± 0.05	0.02 ± 0.02	3.91 ± 1.53
Japanese spanish mackerel	*Scomveromoorus niphonius*	(n = 2)	3.60 ± 1.55	0.003 ± 0.000	0.15 ± 0.02	0.27 ± 0.14	0.02 ± 0.01	0.02 ± 0.01	4.83 ± 0.47
Konoshiro gizzard shad	*Konosirus punctatus*	(n = 2)	1.22 ± 0.50	0.002 ± 0.001	0.14 ± 0.02	0.66 ± 0.04	0.04 ± 0.03	0.07 ± 0.03	6.46 ± 1.04
Largehead hairtail	*Trichiurus lepturus*	(n = 1)	1.26	0.026	0.20	0.13	0.08	0.18	2.48
Marbled rockfish	*Sebastiscus marmoratus*	(n = 1)	2.83	0.001	0.11	0.16	0.13	0.04	3.36
Pacific herring	*Clupea pallasii*	(n = 1)	1.71	0.008	0.29	1.30	0.10	0.42	6.67
Pacific saury	*Cololabis saira*	(n = 1)	0.52	0.006	0.13	0.74	0.04	0.03	3.79
Red seabream	*Pagrus major*	(n = 2)	3.08 ± 0.16	0.003 ± 0.001	0.08 ± 0.03	0.20 ± 0.09	0.04 ± 0.03	0.06 ± 0.02	3.00 ± 1.11
Yellow croaker	*Larimichthys polyactis*	(n = 4)	3.20 ± 1.03	0.005 ± 0.005	0.18 ± 0.06	0.20 ± 0.09	0.02 ± 0.01	0.12 ± 0.20	3.31 ± 0.69
Total	Mean ± SD	(n = 32)	2.58 ± 1.72[b]	0.010 ± 0.026[f]	0.14 ± 0.06[d]	0.54 ± 0.53[c]	0.05 ± 0.04[e]	0.10 ± 0.15[de]	4.87 ± 3.16[a]
Demersal fish									
Armored brotula	*Hoplobrotula armata*	(n = 2)	0.32 ± 0.31	0.024 ± 0.034	0.09 ± 0.04	0.25 ± 0.19	0.10 ± 0.06	0.01 ± 0.00	3.15 ± 0.63
Bastard halibut	*Paralichthys olivaceus*	(n = 4)	2.28 ± 1.27	0.023 ± 0.044	0.09 ± 0.01	0.14 ± 0.04	0.06 ± 0.04	0.16 ± 0.27	2.72 ± 0.51
Black throat sea perch	*Doederleinia berycoides*	(n = 2)	1.72 ± 0.16	0.001 ± 0.001	0.13 ± 0.02	0.08 ± 0.04	0.06 ± 0.00	0.18 ± 0.25	3.82 ± 2.49
Brown sole	*Pleuronectes herzensteini*	(n = 2)	15.45 ± 10.33	0.015 ± 0.018	0.13 ± 0.04	0.15 ± 0.05	0.03 ± 0.00	0.37 ± 0.23	3.28 ± 2.49
Japanese pufferfish	*Takifugu rubripes*	(n = 2)	2.62 ± 1.88	0.004 ± 0.001	0.07 ± 0.01	0.19 ± 0.00	0.10 ± 0.01	0.02 ± 0.01	5.05 ± 0.16
Marbled flounder	*Pleuronectes yokohamae*	(n = 1)	17.63	ND	0.15	0.11	0.07	0.03	3.56
Mi-iuy croaker	*Miichthys miiuy*	(n = 2)	0.50 ± 0.26	0.004 ± 0.000	0.08 ± 0.05	0.19 ± 0.14	0.07 ± 0.05	0.08 ± 0.06	3.55 ± 2.12
Ocellate spot skate	*Okamejei kenojei*	(n = 1)	16.91	0.003	0.11	0.13	0.17	0.01	3.19
Okhostk atka mackerel	*Pleurogrammus azonus*	(n = 1)	1.20	ND	0.21	0.64	0.04	0.02	4.67
Red stingray	*Dasyatis akajei*	(n = 2)	15.80 ± 3.74	0.001 ± 0.001	0.11 ± 0.01	0.30 ± 0.07	0.06 ± 0.04	ND	4.50 ± 0.28
Red tonguesole	*Cynoglossus joyneri*	(n = 1)	8.43	0.002	0.10	0.09	0.01	0.03	3.28
Ridged-eye flounder	*Pleuronichthys cornutus*	(n = 2)	11.33 ± 2.33	0.003 ± 0.003	0.08 ± 0.04	0.18 ± 0.04	0.04 ± 0.00	0.10 ± 0.13	4.28 ± 1.46
Robust tonguefish	*Cynoglossus robustus*	(n = 2)	10.80 ± 1.71	0.002 ± 0.003	0.07 ± 0.00	0.06 ± 0.04	0.02 ± 0.00	0.01 ± 0.00	2.23 ± 0.10
Sailfin sandfish	*Arctoscopus japonicus*	(n = 1)	1.35	0.017	0.13	0.28	0.06	0.07	7.18
Silver pomfret	*Pampus argeneteus*	(n = 2)	0.70 ± 0.15	0.024 ± 0.032	0.15 ± 0.04	0.10 ± 0.06	0.01 ± 0.00	0.01 ± 0.01	3.07 ± 0.64
Whitespotted conger	*Conger myriaster*	(n = 2)	19.48 ± 4.42	0.009 ± 0.010	0.21 ± 0.00	0.32 ± 0.08	0.13 ± 0.03	0.06 ± 0.01	7.04 ± 0.76
Yellow goosefish	*Lophius litulon*	(n = 2)	6.80 ± 1.62	0.001 ± 0.000	0.05 ± 0.01	0.17 ± 0.08	0.08 ± 0.05	0.02 ± 0.01	3.35 ± 1.06
Total	Mean ± SD	(n = 31)	7.28 ± 7.18[a]	0.009 ± 0.019[f]	0.11 ± 0.05[d]	0.19 ± 0.13[c]	0.06 ± 0.04[e]	0.08 ± 0.14[de]	3.85 ± 1.50[b]

Analytical methods

In the laboratory, each fish sample was allowed to reach room temperature and then dissected on a clean ceramic chopping board using a clean ceramic knife. Approximately 20 g of dorsal muscle tissue was taken from fish of each species for analysis. If more than two individual fish of a species had been caught or collected, the tissue between 1 and 10 g was taken from each individual fish and then were mixed. Each tissue sample was washed with distilled water and freeze-dried at -80°C until a constant weight was reached.

Each dry sample was pulverized and homogenized in a jar using a mixer mill. Approximately 1.0 g of the powdered sample was digested in 10 mL of conc. HNO_3 (Suprapur grade; Merck, Darmstadt, Germany) in an acid-cleaned Teflon vessel at room temperature for ~3 hours. A lid was then placed on the vessel and the sample was digested at 80°C for 7 hours, then dried by heating the vessel without the lid on at 100°C for ~3 hours in the clean humhood. This procedure was repeated until a negligible amount of white residue remained. The dry residue was then dissolved in 80 mL of 2% HNO_3, and the solution was filtered through filter paper (Advantec 5C filter paper, 110 mm diameter; Advantec MFS, Dublin, CA, USA), then diluted to 100 mL with 2% HNO_3.

The As, Cd, Cu, Cr, Pb, and Zn concentrations in the sample extracts were determined using an inductively coupled plasma-mass spectrometer (ICP-MS, PerkinElmer, ELAN 6000). The Hg concentrations in the dried tissue samples were measured directly without pretreating the samples using an automated mercury analyzer (Milestone, AMA-254). The accuracy and precision of the analytical procedure were checked by analyzing the certified reference material, ERM-CE278 (for Hg) produced by the Institute for Reference Materials and Measurement and DORM-3 (for heavy metals except Hg) produced by the National Research Council Canada, using the same procedures as were used for the samples. The mean recoveries of the heavy metals in the certified reference material ranged from 92% to 102%. The blank samples were also analyzed by the same procedure as the samples. To prevent contamination during the experiment processes, all procedures were carefully performed at a class 100 clean room. The heavy metal concentrations in the samples are in micrograms per gram wet weight (labeled μg/g later).

Assessment of potential risks

The potential risks of heavy metals in fish tissue to cause harmful effects in the Korean population were evaluated using the provisional maximum tolerable daily intake (PMTDI) that has been suggested by the Joint Food and Agriculture Organization / World Health Organization Expert Committee on Food Additives (JECFA) (WHO 2016) and reference doses (RfD) that have been suggested by the United States Environmental Protection Agency (Onsanit et al. 2010; USEPA 2016). First, the estimated daily intake (EDI) of a metal was calculated and compared with the PMTDI. The EDI (μg/kg·bw/day) is dependent on the metal concentration in fish tissue and the amount of consumed fish, and it was calculated using the following equation (1):

$$EDI = (C_{fish} \times DC_{fish}) / BW \quad (1)$$

where C_{fish} is the mean or max metal concentrations in fish tissue (μg/g), DC_{fish} is the daily fish consumption (g/day) for a Korean adult, and BW is the mean body weight (kg) of a Korean adult.

We also assessed the health risks posed by the consumption of fish using the target hazard quotient (THQ). The THQ indicates the relationship between the amount of toxicant humans are exposed to and the reference dose (RfD), and is part of the USEPA Human Health Risk Assessment approach (Copat et al. 2013; USEPA 2013). The THQ was calculated using the following equation (2):

$$THQ = EDI / RfD \quad (2)$$

Here, THQ of less than 1 was interpreted as indicating that no obvious risks were posed.

Statistical analysis

The heavy metal concentrations in the samples were tested for normality using the Shapiro-Wilk test. The Student's t-test and Mann-Whitnery *U* test were used to identify any significant differences in the accumulation pattern of heavy metals in fish muscle or in the pattern of metal concentrations between pelagic and demersal fishes. Statistical significance was defined as $p < 0.05$. The statistical analyses were performed using SPSS for Window version 11.0 software (SPSS, Chicago, IL, USA).

3. Results and Discussion

Concentration of heavy metals in muscle of wild fish

The concentrations of heavy metals in the muscle of 34 marine wild fishes ($n = 63$) captured from the southern sea of

Korea exclusive economic zone are shown in Table 1. Some metal concentrations in the muscle of wild fish showed large differences with respect to the habitat environment of fish. In the muscle of pelagic fish (17 species, $n = 32$), the mean concentrations of As, Cd, Cr, Cu, Hg, Pb, and Zn were 2.58 μg/g, 0.010 μg/g, 0.14 μg/g, 0.54 μg/g, 0.05 μg/g, 0.10 μg/g, and 4.87 μg/g, respectively. The mean metal concentrations decreased in the order Zn > As > Cu > Cr > Pb > Hg > Cd, and the decreasing order had a statistically significant difference ($p < 0.05$). In the muscle of demersal fish (17 species, $n = 31$), the mean concentrations of As, Cd, Cr, Cu, Hg, Pb, and Zn were 7.28 μg/g, 0.009 μg/g, 0.11 μg/g, 0.19 μg/g, 0.06 μg/g, 0.08 μg/g, and 3.85 μg/g, respectively. Unlike the pelagic fish, the mean metal concentrations decreased in the order As > Zn > Cu > Cr > Hg > Pb > Cd, and the decreasing order had a statistically significant difference ($p < 0.05$).

The As concentrations in demersal fish (especially, in species that live in the bottom sediment) were higher by two or three times magnitude than those in pelagic fish, while the Cr and Cu concentrations were higher by two or three times magnitude in pelagic fish than in demersal fish, with a statistically significant difference ($p < 0.05$, Fig. 2). This result appears to be due to the differences in habitat environment, prey organisms, and uptake rate for each metal between pelagic fish and demersal fish species because metal concentrations in tissues of fish have been found to be strongly related to the habitats, feeding habits, and fat contents of the fish and uptake of heavy metals through the diet could be the major source of metals for many aquatic organisms including invertebrates (Wang 2002; Rainbow 2007; Company et al. 2010; Bilandžić et al. 2011). In addition, Kalantzi et al. (2013) recently reported that wild fish from sites with anoxic substrata accumulate heavy metals such as As and Se from their habitats, but that wild fish from sites with oxic substrata accumulate these elements from their diets. However, the concentrations of other metal except As, Cr, and Cu in the muscle of wild fish did not show any statistically significant difference in relation to the habitat environments (Fig. 2).

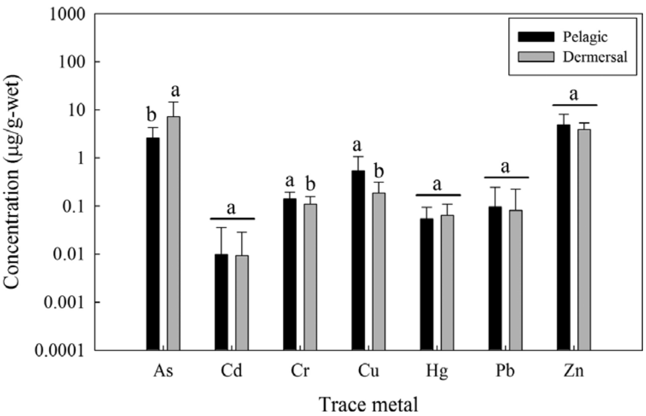

Fig. 2. Comparison of the mean As, Cd, Cr, Cu, Hg, Pb, and Zn concentrations between pelagic and demersal fishes. The error bars represent the standard deviations of the metal concentrations. Concentrations with different letters are significantly different ($p < 0.05$)

Accumulation level for heavy metal in the muscle of wild fish

In order to evaluate the accumulation level of heavy metals in the muscle of 34 wild fishes in the study region, the mean concentrations of heavy metals in each fish species were compared with the regulatory limit for each metal in fish and fishery products of the whole world [reference are shown in Kim and Han (1999), Mok et al. (2009), and Gu et al. (2015)] and with the mean metal concentrations in fish muscle that have been found in other countries (Table 2).

The mean As concentrations in 34 wild fishes were in the range of 0.3–19.5 μg/g. The highest As concentrations were found in *Conger myriaster*. Unfortunately, no regulatory limit for total As in fish has yet been set anywhere in the world, although regulatory limits for inorganic arsenic have been set. The mean As concentration of wild fish in the study region is much higher than that observed in Hong Kong and Iskenderun Bay, while it is of the same order as that observed in Catalonia (references shown in Table 2).

The mean Cd concentrations in 34 wild fishes were in the range of detectable limits (ND) to 0.075 μg/g. The highest Cd concentration was found in *Seriola quinqueradiata*. The mean concentrations in all wild fish except *S. quinqueradiata* were below the regulatory limits for fish and fishery products that are used in a number of other countries (0.05 μg/g in Denmark and Netherlands, 0.1 μg/g in China, 0.2 μg/g in Australia and Korea, 0.5 μg/g in Food and Agriculture Organization (FAO), 1.0 μg/g in New Zealand, and 2.0 μg/g in Hong Kong). In addition, the mean Cd concentration of the wild fish in the study region is much lower than that found in Hong Kong, Mediterranean Sea, the southern Adriatic Sea, and Calicut (Table 2).

The mean Cr concentrations in 34 wild fishes were in the range of 0.05–0.29 μg/g. The highest Cr concentration was found in *Clupea pallasii*. The mean concentrations in all wild fish were below the regulatory limit for fish and fishery products that are used in China (2.0 μg/g). The mean Cr concentration of the wild fish in the study region is much

Table 2. The comparison of As, Cd, Cr, Cu, Hg, Pb, and Zn concentrations in muscle tissue of marine and estuarine fishes from different countries around the whole world. The values in parentheses represent the mean concentration of each heavy metal

Region (Country)	Fish species	Concentration (μg/g-wet weight)							Reference
		As	Cd	Cr	Cu	Hg	Pb	Zn	
Hong Kong and Pearl River Delta (China)	11	0.03–1.53 (0.53)	0.02–0.07 (0.04)	0.20–0.65 (0.44)	0.79–2.26 (1.26)		0.03–8.62 (0.94)	15.2–29.5 (22.3)	Leung et al. (2014)
Mediterranean Sea (Turkey)	12		< 0.01–0.39 (0.10)	0.07–1.48 (0.42)	0.34–7.05 (1.93)		0.14–1.28 (0.48)	3.51–53.5 (10.7)	Türkmen et al. (2009)
Iskenderun Bay (Turkey)	3	0.98–1.74 (1.59)	0.01–0.04 (0.02)	0.32–0.70 (0.56)	4.12–6.24 (5.33)		0.14–0.39 (0.23)	20.8–28.2 (25.5)	Yilmaz et al. (2010)
North Atlantic Ocean	6		ND–0.41		ND–0.89	0.02–0.88	ND–2.40	1.7–10.6	Cronin et al. (1998)
Southern Adriatic Sea (Italy)	3		0.03–0.12 (0.07)			0.15–1.76 (0.84)	0.02–0.10 (0.06)		Storelli et al. (2013)
Catalonia (Spain)	9	0.99–17.8	0.001–0.10			0.04–2.22	0.002–0.25		Falco et al. (2006)
Calicut (India)	13		0.03–0.10 (0.09)	0.10–1.10 (0.62)	0.59–6.50 (3.40)	0.3–0.5** (0.4)**		3.58–60.6 (13.4)	Sankar et al. (2006)
Aegean and Ionian Seas (Greece)	12			0.04–0.27 (0.08)	0.14–2.36 (0.54)	ND–0.1** (0.04)**		2.89–18.8 (6.1)	Kalantzi et al. (2013)
East, West and South Seas (Korea)	35	0.1–65.6 (2.5)	ND–0.11 (0.02)		0.04–5.64 (0.57)	0.002–0.754 (0.07)	ND–0.33 (0.02)	0.52–34.8 (6.1)	Kim et al. (2007)
South Sea (Korea)	34	0.3–19.5 (4.9)	ND–0.075 (0.01)	0.05–0.29 (0.12)	0.06–1.83 (0.36)	0.01–0.17 (0.06)	ND–0.42 (0.09)	2.2–13.3 (4.4)	This study

*ND = Not detected, **concentration in units of μg/kg-wet weight lower than that observed in Hong Kong, Mediterranean Sea, Iskenderun Bay, and Calicut, while it is a little higher than that observed in Aegean and Ionian Seas (Table 2).

The mean Cu concentrations in 34 wild fishes were in the range of 0.06–1.83 μg/g. The highest Cu concentration was found in *Engraulis japonicus*. The mean concentrations in all wild fish were below the regulatory limit for fish and fishery products that are used in Australia (10.0 μg/g) and FAO and New Zealand (30.0 μg/g). The mean Cu concentration of the wild fish in the study region is much lower than that found in Hong Kong, Mediterranean Sea, Iskenderun Bay, and Calicut (Table 2).

The mean Hg concentrations in 34 wild fishes were in the range of 0.01–0.17 μg/g. The highest Hg concentration was found in *Okamejei kenojei*. The mean concentrations in all wild fish were below the regulatory limit for fish and fishery products that are used in a number of other countries (0.3 μg/g in Argentina and Denmark, 0.5 μg/g in Australia, Canada, France, and Korea, 0.7 μg/g in Greece and Italy, and 1.0 μg/g in Netherland, New Zealand, and United States). The mean Hg concentration of the wild fish in the study region is much lower than that observed in the southern Adriatic Sea, while it is much higher than that observed in Aegean and Ionian Seas and Calicut (Table 2).

The mean Pb concentrations in 34 wild fishes were in the range of ND–0.42 μg/g. The highest Pb concentration was found in *C. pallasii*. The mean concentrations in all wild fish except *C. pallasii*, *Pleuronectes herzensteini*, and *Thamnaconus modestus* were below the regulatory limit for fish and fishery products that are used in a number of other countries (0.3 μg/g in Denmark, 0.5 μg/g in Canada, China, FAO, Korea, Netherlands, and New Zealand, 1.5 μg/g in Australia, 2.0 μg/g in England and World Health Organization (WHO)). The mean Pb concentration of the wild fish in the study region is much lower than that observed in Hong Kong, Mediterranean Sea, and Iskenderun Bay, while it is a little higher than that previously observed in Korean coastal oceans (Table 2).

The mean Zn concentrations in 34 wild fishes were in the range of 2.2–13.3 μg/g. The highest Zn concentration was found in *E. japonicus*. The mean concentrations in all wild fish were below the regulatory limit for fish and fishery products that are used in FAO (30.0 μg/g), New Zealand (40.0 μg/g), and England (50.0 μg/g). The mean Zn concentration of the wild fish in the study region is much lower than that observed in Hong Kong, Mediterranean Sea, Iskenderun Bay and Calicut, while it is similar to that observed in Aegean and Ionian Seas and the level previously found in Korean coastal ocean waters (Table 2).

In conclusion, the mean concentrations of each metal except As in fish tissue samples from this study region were much lower than the regulatory limits for fish and fishery products that are used in a number of countries. The mean concentrations of Cd, Cr, Cu, Hg, Pb, and Zn were also relatively low compared with mean concentrations that have been found in marine fish from other countries (including China and Turkey). However, the mean As concentration in wild fish tissue from this study region was much higher than that found in marine fish from other countries.

Assessment of health risk by the consumption of wild fish

Naturally occurring heavy metals in the environment have widely different effects on the human body even at the same concentrations. Metals, such as Fe, Cu, Zn, and Mn, are present at relatively high concentrations in the human body because they are essential elements and play important roles in metabolism and the immune system, whereas some metals, such as Cd, Hg, and Pb, are hazardous to human health, although small amounts can be found in the human body (Bilandžić et al. 2011; Mok et al. 2014). Therefore, we assessed the potential health risks posed to humans by heavy metals consumed in fish caught in the southern sea of Korea.

As mentioned above, we calculated the EDI and THQ using equations (1) and (3) and the calculated EDIs and THQs are shown in Table 3. In this study, the potential health risk for only five metals (Cd, Cr, Cu, Hg, and Zn) were assessed since the PMTDIs of As and Pb established by JECFA were withdrawn in the 79th JECFA meeting held in 2014.

Calculating the EDI, we used the mean and max concentrations of heavy metals in the fish muscle samples (0.01 and 0.15 μg/g, 0.12 and 0.29 μg/g, 0.36 and 2.04 μg/g, 0.06 and 0.17 μg/g, and 4.37 and 16.0 μg/g for Cd, Cr, Cu, Hg, and Zn, respectively), a daily fish consumption of 48.5 g/day for a Korean adult revealed from the Korea National Health and Nutrition Examination Survey (KMOHW 2006; Mok et al. 2009), and a mean body weight of ~64 kg for a Korean adult, from the Korean health statistics for 2008 (KMOHW 2015). The mean and max EDIs for Cd, Cr, Cu, Hg, and Zn were calculated to be approximately 0.01 and 0.11 μg/kg·bw/day, 0.09 and 0.22 μg/kg·bw/day, 0.27 and 1.55 μg/kg·bw/day, 0.05 and 0.13 μg/kg·bw/day, and 3.31 and 12.1 μg/kg·bw/day, respectively. They ranged from 0.05% to 22.5% of the PMTDIs suggested by the Joint Food and Agriculture Organization/

Table 3. Estimated dietary intakes and hazardous level of Cd, Cr, Cu, Hg, and Zn through the consumption of marine fish in Korea

Metals	Mean/Max concentration (μg/g-wet weight)	Daily fish consumption* (g/day)	EDI** (μg/kg·bw/day)	PMTDI† (μg/kg·bw/day)	Hazardous level (%)	RfD# (μg/kg·bw/day)	Target hazard quotient (THQ)	DMPI (g/day)
Cd	0.01/0.15		0.01/0.11	0.83	0.91/13.6	1.0	0.01/0.11	5,300/430
Cr	0.12/0.29		0.09/0.22	None	-	3.0	0.03/0.07	-/660
Cu	0.36/2.04	48.5	0.27/1.55	500	0.05/0.31	None	-	88,900/-
Hg	0.06/0.17		0.05/0.13	0.57	7.96/22.5	None	-	600/-
Zn	4.37/16.0		3.31/12.1	300	1.10/4.04	300	0.01/0.04	4,400/1,200

*Daily consumption of fish reported by Korea National Health and Nutrition Examination Survey (KMOHW 2006)

**EDI : Estimated daily intake calculated from the mean and max concentrations of heavy metal in fish muscle, daily fish consumption, and the mean body weight(bw, ~ 64 kg) of Korean adult (KMOHW 2015)

†PMTDI : Provisional maximum tolerable daily intakes recommended by Joint FAO/WHO Expert Committee on Food Additives (JECFA) (WHO 2016). PMTDI for Cd and Hg were calculated from the provisional tolerable monthly intake (PTMI) and provisional tolerable weekly intake (PTWI) established by the JECFA, respectively

#RfD : Reference dose suggested by integrated risk information systems (IRIS) of United States Environmental Protection Agency (USEPA) (USEPA 2016)

DMPI : Daily maximum permissible intake calculated from the mean and max concentrations of heavy metal in fish muscle, PMTDI (or RfD), and the mean body weight(bw, ~ 64 kg) of Korean adult (KMOHW 2015)

World Health Organization Expert Committee on Food Additives (WHO 2016) and the hazard levels posed by the metals decreased in the order Hg > Cd > Zn > Cu.

We also used THQs to assess the health risks posed to Korean adults through the consumption of wild fish. THQs proposed by the US Environmental Protection Agency is one of the assessment techniques have been used widely around the whole world to assess the risks posed by the consumption of heavy metals in seafood, including fish and shellfish (Storelli 2008). The RfD values that were used (USEPA 2016) and the calculated THQs are shown in Table 3. The mean and max THQs of Cd, Cr, and Zn were all less than 1.0 and the hazard levels posed by the metals decreased in the order Cd > Cr > Zn. Based on the overall results of risk assessment, the daily intake of metals via consumption of wild fish in the study region do not pose a hazard to the health of Koreans.

On the other hand, the amounts of fish consumption by Koreans show a great difference according to individual persons and region and increase every year. Especially, Koreans that live in seaside districts consume a large amount of fish at one time although the mean of daily fish consumption (48.5 g/day) reported from the Korea National Health and Nutrition Examination Survey is very small. Therefore, we calculated the daily maximum permissible intake (DMPI) in this study to ensure the safety of fish consumption by Koreans. The DMPI was calculated using the following equation (3):

$$DMPI = (PMTDI \text{ or } RfD \times BW) / C_{fish} \quad (3)$$

Based on the mean and max concentrations of Cd, Cr, Cu, Hg, and Zn in the muscle of wild fish (C_{fish}), TMTDI or THQ, and the mean body weight (kg) of a Korean adult (BW), the DMPI for wild fish were estimated to be approximately 430 g/day (Table 3). Therefore, we suggest that more than 430 g/day of wild fish consumption is likely to have a significant influence on human health.

4. Conclusions

The concentrations of As, Cd, Cr, Cu, Hg, Pb, and Zn in the muscle of 34 wild fish caught from the southern sea of Korea in 2007 and 2008 were measured. The metal concentrations in pelagic fish decreased in the order Zn > As > Cu > Cr > Pb > Hg > Cd, whereas the metal concentrations in demersal fish decreased in the order As > Zn > Cu > Cr > Hg > Pb > Cd. In addition, the As concentrations in demersal fish were much higher fish than those in pelagic fish, while the Cr and Cu concentrations were much higher in pelagic fish than in demersal fish due to differences in habitat environment, prey organisms, and metal uptake rate. Although the mean concentrations of all metals except As in wild fish were below the regulatory limit for fish and fishery products applied in a number of countries and were much lower than those observed in other countries, the mean As concentration was relatively higher than that found in other countries. Considering the results of risk assessment by fish consumption, the consumption of wild fish caught from the study region does not pose any adverse risks to human health. However, the daily maximum permissible intakes of marine wild fish in the study region were calculated to be approximately 430 g/day. Therefore, an appropriate intake limit for wild fish caught from the southern sea of Korea is necessary to protect human health in the future.

Acknowledgements

This work was supported by a research grant from the National Institute of Fisheries Science (NIFS, R2017053). We would like to thank many of our colleagues who helped in the sample collection and performed heavy metal analyses.

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