Ecotoxicology (2015) 24:1583–1592
DOI 10.1007/s10646-015-1451-7

Heavy metals in wild marine fish from South China Sea: levels, tissue- and species-specific accumulation and potential risk to humans

Jin-Ling Liu[1,5] · **Xiang-Rong Xu**[1] · **Zhen-Hua Ding**[2] · **Jia-Xi Peng**[1,4] · **Ming-Hua Jin**[2] · **You-Shao Wang**[3] · **Yi-Guo Hong**[3] · **Wei-Zhong Yue**[3]

Accepted: 21 March 2015

Abstract Heavy metal pollution in marine fish has become an important worldwide concern, not only because of the threat to fish in general, but also due to human health risks associated with fish consumption. To investigate the occurrence of heavy metals in marine fish species from the South China Sea, 14 fish species were collected along the coastline of Hainan China during the spring of 2012 and examined for species- and tissue-specific accumulation. The median concentrations of Cd, Cr, Cu, Zn, Pb and As in muscle tissue of the examined fish species were not detectable (ND), 2.02, 0.24, 2.64, 0.025, and 1.13 mg kg^{-1} wet weight, respectively. Levels of Cu, Zn, Cd and Cr were found to be higher in the liver and gills than in muscle, while Pb was preferentially accumulated in the gills. Differing from other heavy metals, As did not exhibit tissue-specific accumulation. Inter-species differences of heavy metal accumulation were attributed to the different habitat and diet characteristics of marine fish. Human dietary exposure assessment suggested that the amounts of both Cr and As in marine wild fish collected from the sites around Hainan, China were not compliant with the safety standard of less than 79.2 g d^{-1} for wild marine fish set by the Joint FAO/WHO Expert Committee on Food Additives. Further research to identify the explicit sources of Cr and As in marine fish from South China Sea should be established.

Keywords Heavy metals · Accumulation · Wild marine fish · South China Sea · Risk assessment

Introduction

In recent years, the worldwide demand for fish has been growing rapidly because fish is an important food source to human populations. Fish can supply both proteins and omega-3 polyunsaturated fatty acids, which are well-known for significantly reducing cholesterol levels and maintaining healthy immune systems (Copat et al. 2012). However, heavy metal pollution in fish has become an important worldwide concern, not only because of the threat to fish health, but also due to the health risks associated with contaminated fish consumption. Heavy metals, such as copper (Cu), zinc (Zn), iron (Fe) and manganese (Mn) are essential nutrients, whereas cadmium (Cd), lead (Pb) and mercury (Hg) are toxic, even at very low levels. The essential metals play important roles in biological systems, however, they can cause toxic effects when the metal intakes are excessively elevated (Tuzen 2003; Celik and Oehlenschlager 2007). As fish are constantly exposed to chemicals in contaminated water, food, or sediment, they may accumulate large quantities of certain metals. As a result, fish have been utilized as indicators of heavy metal contamination in aquatic environments (Burger et al. 2002). The uptake of heavy metals in fish has two

✉ Xiang-Rong Xu
xuxr@scsio.ac.cn

[1] Key Laboratory of Tropical Marine Bio-resources and Ecology, South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou 510301, China

[2] College of the Environment & Ecology, Xiamen University, Xiamen 361005, China

[3] State Key Laboratory of Tropical Oceanography, South China Sea Institute of Oceanology, CAS, Guangzhou 510301, China

[4] University of Chinese Academy of Sciences, Beijing 100049, China

[5] School of Earth Sciences, China University of Geosciences, Wuhan 430074, China

pathways: the digestive tract by diet exposure and the gill surface by water exposure (Ptashynski et al. 2002). Upon entry, heavy metals are further transferred via blood to other target organs such as the liver and kidney. It is important to monitor the tissues of common fish species for heavy metal concentration as it will provide an indication of heavy metal contamination status in aquatic environments. This metric is especially important due to bioaccumulation, which has the largest potential impact on humans who are tertiary consumers (Hillwalker et al. 2006).

China is the largest fish producer and exporter in the world with 47.4 million metric tons produced, accounting for 35 % of global fish production in 2010 (FAO 2012). The South China Sea (SCS), abundant in tropical fish resources with the largest species variety and the greatest production, contributed 25 % (3.6 million metric tons) to Chinese total marine capture fishery production (FAO 2013). The captured marine fish are not only consumed by the countries nearby SCS, but also exported to the other countries in the world. However, increased industrialization, urbanization and other anthropogenic activities have aggravated marine pollution levels in SCS (NBO 2012). Heavy metals discharged into the marine environment (Pan and Wang 2012; Wang et al. 2013; Liu et al. 2014a, b) can damage marine species diversity as well as ecosystems (Ebrahimpour et al. 2011), which assimilates into human consumers resulting in health risks. Therefore, the determination of metal content in the tissues and organs of fish, which indicates the concentrations of metals in water and their accumulation in food web is of significance (Pintaeva et al. 2011).

To accomplish this objective, 14 marine fish species were collected from SCS and heavy metal levels in muscle, liver, and gill tissue of the different fish species were analyzed. The analysis provides information to (1) investigate the presence of heavy metals in fish species along the coastline of Hainan, (2) examine species and tissue-specific accumulation of heavy metals in marine fish, and (3) evaluate the public health risks associated with consuming fish harvested from these areas by estimating daily and weekly intakes and by comparing them with the acceptable daily intake (ADI) and the provisional tolerance weekly intake (PTWI) recommended by various authorities.

Materials and methods

Study area and fish sample collections

Collection of marine wild fish samples was conducted during the spring of 2012 at Hainan Island (Fig. 1), which is the biggest island (33,210 km^2 of land area) in the SCS. It is a major marine aquaculture base with annual production of approximately 990,000 metric tons, accounting for 6.8 % of the total marine production in China in 2010 (FAO 2013). Aquaculture has been expanding fast in Hainan Island to meet the seafood demands from European Union, Southeast Asia and China over the past decades.

Fresh fish was collected in the fishing pier along coastal areas of Hainan. A total of 94 fish samples, comprising 14 species, were collected from the local fishermen at the capturing day. Each sample was cleaned and kept in clean plastic bags separately, then stored in a big ice box and immediately transferred to the laboratory to be frozen at −20 °C until dissection and analysis. Characteristics of the collected fish species from coastal areas of Hainan are listed in Table 1.

Determination of heavy metals and QA/QC

Both fish length and weight were measured before dissection. The gill, liver, and muscle were dissected using clean scalpels and scissors. After the dissection, the tissues were freeze-dried and ground. Water content of individual samples were determined by difference in wet and dry weight. Approximately 200 mg of sample were weighed into digestion flasks followed by 3 mL concentrated nitric acid (65 %). The digestion flasks were then put on a hot plate set (MK-10G, Allsheng Instruments Company Limited, China) at 80 °C for 24 h until all the tissues were dissolved (Zhang and Wang 2012). After cooling at room temperature, all digested samples were diluted with Milli-Q water to 50 mL.

Standard solutions were prepared from stock standard solutions of the metals (Merck, multi-element standard, Germany). Cd, chromium (Cr), Cu, Zn, Pb and arsenic (As) in the samples, were determined by inductively coupled plasma mass spectrometry (DRC-e, PerkinElmer Limited, USA). All the samples were taken in triplicate and all measurements were run in triplicate for standard and samples. Accuracy and precision of the analytical procedure were tested with a reference material (DORM-2, dogfish muscle, National Research Council, Canada). The mean recoveries of Cd, Cr, Cu, Zn, Pb, and As were 98.6, 104.3, 100.8, 89.2, 96.5, and 107.0 %, respectively. The relative standard deviations of duplicate samples were less than 10 %.

Risk assessment method

The human risk assessment was conducted using ADI, PTWI previously established by the Joint FAO/WHO Expert Committee on Food Additives (JECFA) (FAO/WHO 2010), and reference dose (RfD) by the United

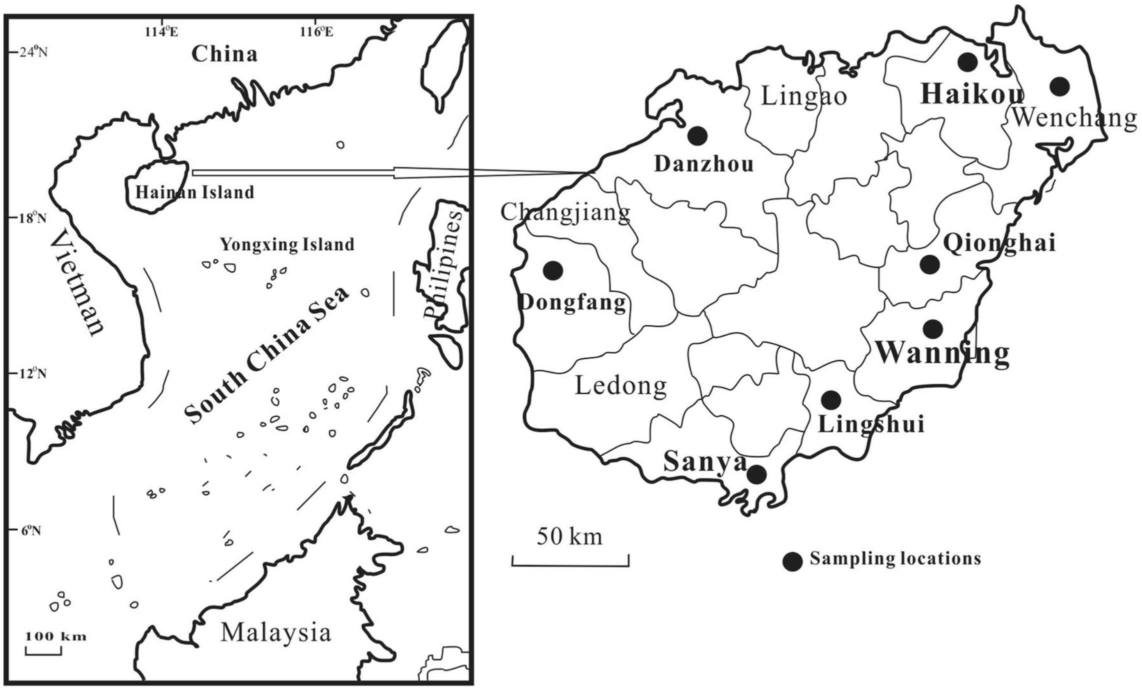

Fig. 1 Map of the study areas

Table 1 Fish species collected from coastal areas of Hainan coast

Common name	Scientific name	*n*	Feeding mode	Diet	Length (cm)	Weight (g)
Crimson snapper	*Lutjanus erythropterus*	8	Carnivorous	Other fish, crustaceans, benthic invertebrates	19–30	220–520
Orbfish	*Ephippus orbis*	4	Carnivorous	Small fish, benthic invertebrates	20–29	250–480
Blood porgy	*Parargyrops edita*	12	Carnivorous	Small fish, polychaetes, cephalopoda	10–18	37–160
Goldsilk seabream	*Sparus berda*	6	Carnivorous	Small fish, polychaetes, cephalopoda	17–33	160–660
Yellowfin filefish	*Navodon xanthopterus*	6	Filter feeder	Zooplankton, plankton, benthic organism	11–50	80–1390
Redgill emperor	*Lethrinus rubrioperculatus*	8	Carnivorous	Crustaceans, fish, mollusks,echnoderms	17–24	60–250
Rabbitfish	*Siganus fuscescens*	4	Omnivorous	Alage, small invertebrates	16–28	230–440
Scomber	*Pneumatophorus japonicas*	8	Carnivorous	Small fish, copepods, cuttlefish	24–25	259–270
Jarbua terapon	*Therapon jarbua*	8	Carnivorous	Small fish, crustaceans, benthic invertebrates	12–32.5	16–510
Spotted grouper	*Epinephelus areolatus*	4	Carnivorous	Fish, benthic invertebrates	24–25	390–410
Spinefoot	*Siganus guttatus*	10	Herbivorous	Alage, small vascular plant	13–24	50–310
Speckled tongue sole	*Cynoglossus robustus*	8	Bottom feeder	Benthic invertebrates	13–23	30–200
Scomberoides lysan	*Chorinemus lysan*	4	Carnivorous	Small fish, crustaceans	17–25	70–200
Razorbelly scad	*Caranx kalla*	4	Carnivorous	Primary invertebrates	14–15	60–90

States Environmental Protection Agency (USEPA 2005), respectively.

The estimated daily intake (*EDI*) (μg kg^{-1} d^{-1}) was calculated using the following Eq. (1):

$$EDI = [C_{\text{fish}} \times IR_{\text{fish}}]/BW \tag{1}$$

where C_{fish} is the average heavy metal concentration in fish muscle (μg g^{-1} wet weight), IR_{fish} is daily fish consumption (g d^{-1}), *BW* is the average body weight (kg) of the target population.

The hazard quotient (HQ) was calculated by the following Eq. (2):

$$\text{HQ} = EDI/\text{RfD} \tag{2}$$

There would be no obvious risk if the HQ value is less than 1.

Statistical analysis

Statistical analysis was performed using SPSS 16.0 for Windows (SPSS Inc., Chicago, USA). Data were grouped according to species and plotted on graphs to see their distributions. One-way analysis of variance (ANOVA) was used to test for differences in metal concentrations of different species and tissues. The level of significance was acceptable at $p < 0.05$. All sample values were blank-subtracted and expressed as mg kg^{-1} wet weight.

Results and discussion

Levels of heavy metals in fish muscle

As shown in Table 2, regardless of fish species, the mean concentrations of Cd, Cr, Cu, Zn, Pb and As in fish muscles were 0.003 ± 0.001, 2.20 ± 0.12, 0.35 ± 0.03, 2.86 ± 0.19, 0.03 ± 0.002, 2.17 ± 0.28 mg kg^{-1} respectively. The median concentrations of Cd, Cr, Cu, Zn, Pb, and As in fish muscles were ND, 2.02, 0.24, 2.64, 0.025, and 1.13 mg kg^{-1}, respectively. A previous study had shown that average concentrations of As, Cd, Cr, Cu, Pb and Zn in sediments of the Hainan coast were 5.50, 0.03, 16.1, 4.48, 16.1, and 21.9 mg kg^{-1}, respectively (Xia et al. 2011). Based on these data, the bioconcentration factors (BCFs) of Cd, Cr, Cu, Zn, Pb and As in fish were 0.10, 0.14, 0.08, 0.13, 0.002, and 0.39, respectively. BCFs ranked in decreasing order of magnitude results in the following: As > Cr > Zn > Cd > Cu > Pb. All the BCF values of heavy metals in marine fish were less than 1.

Compared with other studies, the results in the present study were lower than the previously reported values of Cu, Pb, Cd and Zn in fish species from freshwater (Table 3) (Ip et al. 2005; Rahman et al. 2012; Yi and Zhang 2012), and comparable to those in marine fish species from the Gulf of Oman (de Mora et al. 2004), Adriatic Sea (Bilandžić et al. 2011), and Aegean and Mediterranean Sea (Türkmen et al. 2009), but higher than the concentrations of Cr and As in freshwater fish species from Pearl River and Bangshi River (Ip et al. 2005; Rahman et al. 2012). However, these comparisons should be used with caution due to differences in fish species and habitats between the studies. The levels of Cu, Pb and Cd in the fish from the previously cited studies were lower than the values in freshwater fish in the present study. This result can be partially attributed to the differences in metal uptake and accumulation by fish in marine and freshwater environments, and these differences includes ambient physicochemical factors and physiological responses. Dietary uptake is the predominant pathway of metal accumulation in marine fish while the uptake of dissolved metal from the ambient environment may be an important pathway for freshwater fish in metal uptake and accumulation (Wang and Rainbow 2008).

The elevated levels of Cr and As obtained from marine fish in Hainan are likely caused by agricultural use and geogenic origin. Due to the underdeveloped industrial sector, Hainan has a primarily tourist and agriculture-based economy. Inorganic As was often used in agriculture as an insecticide, herbicide, fungicide, desiccant, defoliant, and animal feed additive (Cheung et al. 2008). Due to geogenic origin and anthropogenic activity, high levels of Cr and As have been found in mangrove sediment of Hainan and might pose a great risk to fish living there. (Vane et al. 2009; Qiu et al. 2011; Liu et al. 2014b).

Tissue-specific accumulation of heavy metals in fish

The results of heavy metal bioaccumulation in the tissues of 14 fish species are listed in Table 2. ANOVA analyses revealed that significant variations in bioaccumulation ($p < 0.05$) were found for Cd, Cr, Cu, Zn, and Pb among different tissues. The levels of As did not show any differences between tissues ($p > 0.05$). Overall concentrations of Cu, Zn, Cd and Cr in muscles, irrespective of species, were considerably lower than those in liver and gill, which indicates that heavy metals were preferentially accumulated in liver and gill. This finding suggests heavy metal burden in fish and the existence of major routes of heavy metal uptake from the aquatic environment (Tapia et al. 2012). It has been observed that different tissues of fish may have distinct affinities for heavy metal accumulation due to their differing physiological functions (Tapia et al. 2012). In this study, the elevated levels of Cu, Cd, Zn, and Cr in liver, relative to other tissues, are directly associated with the metabolism and indicates that food consumption is the major exposure route of these metals. This can be demonstrated by the fact that the liver is generally considered to have a strong metal accumulative potential owing to the activity of metal-binding proteins such as metallothioneins. These proteins can bind Cu, Cd, and Zn, but not Pb, resulting in elevated levels of metals in liver (Uysal et al. 2009; Tapia et al. 2012). Moreover, liver is the dominant site for detoxification of contaminants and received metals from various routes of absorption (Vaseem and Banerjee 2013).

For most fish species, the highest values of Pb were found in the gills compared to the other two studied tissues. Gills are an important organ of interest in terms of their ability to uptake heavy metals from the water due to the metal-binding sites located at the tissue's surface (Wang and Rainbow 2008). Thus the high levels of Pb in the gills are likely related to the contribution of water uptake rather than food. Another reason for elevated metal accumulation

Table 2 Concentrations of heavy metal (mg kg^{-1} wet weight) in tissue of wild marine fish from Hainan coast

Fish		Cd	Cr	Cu	Zn	Pb	As
Crimson snapper	Muscle	ND	1.47 ± 0.25	0.21 ± 0.01	1.54 ± 0.24	0.02 ± 0.004	1.16 ± 0.31
	Liver	0.16 ± 0.03	2.17 ± 0.39	0.79 ± 0.19	6.37 ± 0.98	0.04 ± 0.007	3.21 ± 1.05
	Gill	ND	3.68 ± 0.62	0.58 ± 0.16	10.8 ± 1.92	0.07 ± 0.007	4.72 ± 1.45
Orbfish	Muscle	0.001 ± 0.001	2.27 ± 0.23	0.54 ± 0.06	2.92 ± 0.11	0.05 ± 0.02	1.51 ± 0.01
	Liver	0.11 ± 0.002	3.41 ± 0.21	1.89 ± 0.51	11.8 ± 0.92	0.04 ± 0.001	0.96 ± 0.09
	Gill	0.001 ± 0.002	2.85 ± 0.35	0.93 ± 0.006	10.2 ± 0.46	0.05 ± 0.02	0.81 ± 0.09
Blood porgy	Muscle	ND	2.44 ± 0.26	0.39 ± 0.061	4.08 ± 0.67	0.04 ± 0.004	1.49 ± 0.33
	Liver	0.07 ± 0.01	3.91 ± 0.72	2.71 ± 0.92	19.1 ± 3.45	0.50 ± 0.25	2.35 ± 0.43
	Gill	0.06 ± 0.02	2.37 ± 0.19	0.63 ± 0.09	19.1 ± 1.79	0.13 ± 0.02	2.79 ± 0.48
Goldsilk seabream	Muscle	ND	1.65 ± 0.18	0.23 ± 0.01	1.84 ± 0.20	0.04 ± 0.02	0.91 ± 0.12
	Liver	0.09 ± 0.02	1.88 ± 0.34	1.43 ± 0.40	12.7 ± 0.68	0.10 ± 0.02	1.49 ± 0.42
	Gill	0.001 ± 0.001	2.14 ± 0.09	0.35 ± 0.06	11.7 ± 2.35	1.64 ± 0.99	0.72 ± 0.16
Yellowfin filefish	Muscle	ND	1.38 ± 0.18	0.07 ± 0.01	1.45 ± 0.13	0.03 ± 0.01	6.48 ± 2.14
	Liver	0.29 ± 0.14	2.06 ± 0.36	1.24 ± 0.12	12.5 ± 0.79	0.14 ± 0.06	4.21 ± 1.95
	Gill	0.03 ± 0.01	3.19 ± 0.24	1.05 ± 0.33	11.9 ± 1.12	0.21 ± 0.03	1.73 ± 0.38
Redgill emperor	Muscle	0.006 ± 0.003	2.57 ± 0.35	0.19 ± 0.02	1.92 ± 0.22	0.03 ± 0.003	4.07 ± 0.78
	Liver	0.45 ± 0.14	3.25 ± 0.38	1.62 ± 0.05	10.3 ± 1.95	0.06 ± 0.008	3.95 ± 0.73
	Gill	0.05 ± 0.02	5.19 ± 1.25	0.81 ± 0.11	16.2 ± 2.02	0.12 ± 0.03	3.88 ± 0.79
Rabbitfish	Muscle	0.002 ± 0.001	4.36 ± 1.60	0.28 ± 0.02	3.43 ± 0.37	0.05 ± 0.018	0.48 ± 0.03
	Liver	0.16 ± 0.08	1.52 ± 0.06	2.27 ± 0.67	13.3 ± 0.55	0.11 ± 0.02	1.00 ± 0.07
	Gill	0.10 ± 0.06	3.31 ± 0.41	0.90 ± 0.24	13.5 ± 2.67	0.22 ± 0.03	1.07 ± 0.007
Scomber	Muscle	0.012 ± 0.002	2.11 ± 0.18	0.49 ± 0.06	3.13 ± 0.09	0.02 ± 0.002	0.59 ± 0.03
	Liver	0.61 ± 0.01	1.69 ± 0.008	1.68 ± 0.002	24.9 ± 2.29	0.06 ± 0.009	1.36 ± 0.03
	Gill	0.05 ± 0.02	2.47 ± 0.17	0.53 ± 0.05	20.3 ± 1.91	0.67 ± 0.14	0.79 ± 0.02
Jarbua terapon	Muscle	ND	1.90 ± 0.02	0.19 ± 0.02	3.18 ± 0.18	0.03 ± 0.006	1.32 ± 0.09
	Liver	0.19 ± 0.01	2.66 ± 0.25	0.82 ± 0.004	8.82 ± 0.45	0.07 ± 0.001	2.91 ± 0.56
	Gill	0.007 ± 0.002	3.28 ± 0.25	0.42 ± 0.02	16.9 ± 0.77	0.36 ± 0.09	0.95 ± 0.05
Spotted grouper	Muscle	ND	1.66 ± 0.21	0.17 ± 0.03	1.63 ± 0.27	0.05 ± 0.018	0.86 ± 0.13
	Liver	0.16 ± 0.02	2.57 ± 0.47	1.32 ± 0.08	12.2 ± 2.02	0.07 ± 0.02	1.23 ± 0.006
	Gill	0.07 ± 0.002	3.43 ± 0.58	0.79 ± 0.28	9.95 ± 0.99	0.04 ± 0.005	0.74 ± 0.04
Spinefoot	Muscle	0.008 ± 0.005	1.82 ± 0.31	0.42 ± 0.15	2.72 ± 0.75	0.03 ± 0.007	0.49 ± 0.12
	Liver	0.51 ± 0.27	1.48 ± 0.25	1.20 ± 0.28	8.99 ± 2.21	0.23 ± 0.05	1.02 ± 0.24
	Gill	0.02 ± 0.01	2.00 ± 0.07	0.52 ± 0.09	9.65 ± 0.52	0.10 ± 0.03	0.75 ± 0.11
Speckled tongue sole	Muscle	0.004 ± 0.003	2.15 ± 0.21	0.46 ± 0.11	2.53 ± 0.31	0.03 ± 0.004	6.99 ± 0.85
	Liver	0.23 ± 0.06	3.60 ± 0.57	2.49 ± 0.68	15.4 ± 1.48	0.41 ± 0.13	1.69 ± 0.22
	Gill	0.03 ± 0.004	3.69 ± 0.13	0.74 ± 0.13	20.9 ± 4.59	0.17 ± 0.03	1.54 ± 0.17
Scomberoides lysan	Muscle	ND	2.36 ± 0.20	0.94 ± 0.09	3.11 ± 0.15	0.04 ± 0.01	0.99 ± 0.07
	Liver	0.09 ± 0.008	3.13 ± 0.72	1.29 ± 0.05	13.7 ± 1.94	0.04 ± 0.006	1.74 ± 0.027
	Gill	0.13 ± 0.06	4.39 ± 0.95	1.35 ± 0.09	25.4 ± 7.49	0.07 ± 0.009	2.69 ± 0.72
Razorbelly scad	Muscle	0.003 ± 0.002	4.20 ± 0.03	0.55 ± 0.11	8.07 ± 0.96	0.04 ± 0.01	2.12 ± 0.56
Guideline							
EC (2006)		0.05				0.3	2
GB2762-2012 (MOH 2012)		0.1	2	50	50	0.5	1[a]

ND not detectable

[a] Inorganic As : total As = 1:10 United States Food and Drug Administration (USFDA) (1993)

in the gills may be due to high density of chloride cells capable of picking up cations, such as heavy metal ions (Costa and Fernandez 2002).

Muscle tissue is commonly regarded to have a low accumulation ability for heavy metals (Tapia et al. 2012). However, this is not always the case. Cr (in *Siganus*

Table 3 Heavy metal levels in fish muscles from different locations worldwide

	Location	Cu	Zn	Pb	Cd	Cr	As	Reference
Fresh	Bangshi River[a] (Bangladesh)	8.33–43.18	42.83–418	1.76–10.27	0.09–0.87	0.47–2.07	1.97–6.24	Rahman et al. (2012)
	Yangtze River[b] (China)	0.771–1.22	2.8–7.55	0.21–0.81	0.0457–0.115	0.10–0.24	NA	Yi and Zhang (2012)
	Pearl River[b] (China)	0.15–7.55	8.78–30.3	0.09–30.7	0.01–0.13	0.11–4.27	NA	Ip et al. (2005)
Marine	Aegean and Mediterranean Sea[b] (Turkey)	0.51–7.05	3.51–53.5	0.21–1.28	<0.01–0.39	0.07–1.48	NA	Türkmen et al. (2009)
	Adriatic Sea[b] (Country for consistency)	0.13–1.47	NA	0.01–0.02	0.002–0.006	NA	0.43–5.91	Bilandžić et al. (2011)
	Gulf of Oman[a] (Oman)	0.24–19.5	1.82–67.3	NA	NA	ND–0.077	0.83–14.4	de Mora et al. (2004)
	Hainan coastal area, South China Sea[b] (China)	0.07–0.94	1.45–8.07	0.02–0.05	ND–0.012	1.38–4.36	0.48–6.99	This study

ND not detectable, *NA* not analyzed

[a] Values present the ranges expressed as mg kg^{-1} dry weight

[b] Values present the ranges expressed as mg kg^{-1} wet weight

fuscescens) and As (in *Navodon xanthopterus*, *Lethrinus rubrioperculatus*, *Cynoglossus robustus* and *Ephippus orbis*) concentrations in the marine fish muscles in the present study were higher than those in gill and liver. A similar phenomenon of higher metal (Cd) concentration in the muscle of *C. carassius* than that in gill and liver was also found in a previous study (Uysal et al. 2009). This may be due to the distinct distribution pattern of heavy metals among different fish species. The explicit reason for elevated metal concentrations in muscle needs further investigation.

Species-specific accumulation of heavy metal in fish

As muscle tissues have a higher contribution to overall biomass than the liver and gills, heavy metals in muscles were used for inter-species comparison in the present study. ANOVA analyses indicated significant variations ($p < 0.05$) of Cd, Cr, Cu, Zn, and As in muscles of different fish species. Species-specific accumulation of heavy metals in muscles of fish is shown in Table 2. Carnivorous fish *Pneumatophorus japonicas* had the highest concentration of Cd. The lowest levels of Cr, Cu, and Zn were found in omnivorous fish *N. xanthopterus* which live at the bottom water, while the highest levels of Cr, Cu, and Zn were found in *S. fuscescens* (omnivorous, bottom), *Chorinemus lysan* (carnivorous, middle), and *Caranx kalla* (carnivorous, middle), respectively. Similarly, the highest level of Pb was found in omnivorous fish (*S. fuscescens*, bottom), while the lowest in carnivorous fish *Lutjanus erythropterus* (bottom) and *P. japonicas* (pelagic). These results revealed that feeding habits and habitat were important factors affecting the accumulation of heavy metals in fish. In order to clarify impacts of the feeding habit and habitat on metal accumulation in fish, fish species were categorized by feeding habit into five groups (carnivorous, omnivorous, herbivorous, filter feeder and bottom feeder). As shown in Fig. 2, the highest concentrations of Cr, Zn, and Pb were found in omnivorous fish, but Cu and As exhibited the highest values in bottom feeder fish. Filter feeder fish had the lowest levels of Cr, Cu, Zn, and Pb, but a higher level of As. The results indicated no obvious relationship between trophic levels and bioaccumulation of heavy metals. However, the high levels of Cu and As in the bottom feeder fish demonstrated that feeding habits and habitat play important roles in metal accumulation in fish (Zhao et al. 2012; Monikh et al. 2013). Bottom sediment is a sink and source of heavy metals in marine environment

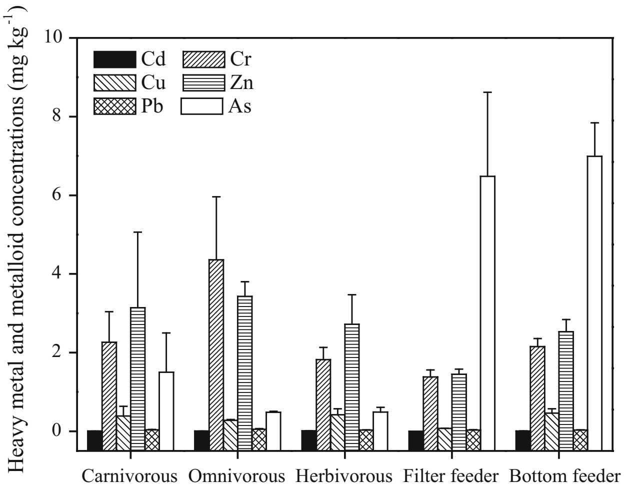

Fig. 2 Comparison of heavy metal concentrations in wild marine fish with different functional groups

Table 4 Pearson correlation coefficient (*R*) for relationships between heavy metal concentrations and fish size (weight and length)

Species	Cd	Cr	Cu	Zn	As	Pb	Species	Cd	Cr	Cu	Zn	As	Pb
Chorinemus lysan							*Therapon jarbua*						
Length	−0.382	−0.734**	−0.583*	−0.463	−0.357	−0.21	Length	0.137	0.535**	0.004	0.159	0.372	−0.358
Weight	−0.382	−0.734**	−0.583*	−0.463	−0.357	−0.21	Weight	0.137	0.535**	0.004	0.159	0.372	−0.358
Cynoglossus robustus							*Siganus guttatus*						
Length	−0.123	−0.332	−0.420*	−0.447*	0.239	0.172	Length	−0.165	−0.253	−0.305	−0.171	−0.176	0.14
Weight	−0.243	−0.337	−0.293	−0.389	0.305	0.267	Weight	−0.141	−0.218	−0.283	−0.143	−0.14	0.101
Caranx kalla							*Siganus fuscescens*						
Length	−1**	−0.604	−0.999**	0.999**	−1**	−0.998**	Length	−0.684*	−0.555	0.214	−0.381	0.052	−0.474
Weight	−1**	−0.604	−0.998**	0.999**	−1**	−0.998**	Weight	−0.684*	−0.555	0.214	−0.381	0.052	−0.474
Epinephelus areolatus							*Sparus berda*						
Length	0.158	0.686*	0.411	−0.086	−0.381	0.648*	Length	0.246	−0.767**	−0.256	−0.278	0.089	−0.183
Weight	0.158	0.686*	0.411	−0.086	−0.381	0.648*	Weight	0.227	−0.778**	−0.193	−0.232	0.212	−0.101
Ephippus orbis							*Pneumatophorus japonicas*						
Length	0.046	0.689*	0.435	0.216	0.348	0.829**	Length	0.003	0.329	−0.128	−0.024	0.147	0.252
Weight	0.046	0.689*	0.435	0.216	0.348	0.829**	Weight	0.019	−0.16	0.025	0.005	−0.029	−0.047
Lutjanus erythropterus							*Parargyrops edita*						
Length	0.289	0.529**	0.376	0.461*	0.466*	0.403	Length	0.189	−0.611**	−0.424**	−0.25	−0.585**	−0.417*
Weight	0.277	0.17	0.176	0.328	0.263	0.231	Weight	0.287	−0.377*	−0.153	−0.139	−0.338*	−0.08
Lethrinus rubrioperculatus							*Navodon xanthopterus*						
Length	0.108	−0.543**	−0.123	−0.243	−0.06	−0.459*	Length	−0.274	0.322	−0.006	0.047	0.514*	0.299
Weight	0.081	−0.423*	−0.129	−0.198	−0.028	−0.359	Weight	−0.278	0.333	−0.017	0.046	0.507*	0.307

** $p < 0.01$; * $p < 0.05$

(Dalman et al. 2006; Monikh et al. 2013). The bottom feeder fish live close to sediment and are easily exposed to higher concentrations of heavy metals.

Relationships between heavy metal concentrations and fish size (length and weight) are listed in Table 4. Significant negative correlations were found between fish length and Cr in *C. lysan* ($p < 0.01$) and *Sparus berda* ($p < 0.01$), Cu in *C. lysan* ($p < 0.05$) and *C. kalla* ($p < 0.01$), Zn in *C. robustus* ($p < 0.05$), As in *Parargyrops edita* ($p < 0.01$) and *C. kalla* ($p < 0.01$), Pb in *L. rubrioperculatus* ($p < 0.05$) and *C. kalla* ($p < 0.01$), Cd in *S. fuscecsens* ($p < 0.05$) and *C. kalla* ($p < 0.01$). Significant positive correlations were found between fish length and Cr in *Epinephelus areolatus* ($p < 0.05$) and *E. orbis* ($p < 0.05$), Zn in *L. erythropterus* ($p < 0.05$) and *C. kalla* ($p < 0.01$), As in *N. xanthopterus* ($p < 0.05$), Pb in *E. orbis* ($p < 0.01$). Similar correlations were found between the heavy metal concentrations in fish tissue and weight (Table 4). No significant relationships were found between fish size and heavy metal concentrations in *P. japonicas* and *Siganus guttatus*. Although both negative and positive relationships between fish sizes and metal levels were found in statistically significant cases, the negative relationship between fish size and heavy metal concentrations is present in most cases in this study and has been reported in previous studies (Canli and Atli 2003; Yi and Zhang 2012; Monikh et al. 2013). These results demonstrated the growth dilution and elimination of heavy metal accumulation in fish (Zhang and Wang 2007). It is well accepted that metabolic activity of fish changes with different sizes. Generally, metabolic activities of young individuals are higher than those of older individuals (Widianarko et al. 2000; Monikh et al. 2013). Moreover, the physiological kinetic parameters such as the uptake rate and ingestion rate were also found to be negatively correlated with marine fish size (Zhang and Wang 2007). Therefore, concentrations of heavy metals in the marine fish decreased with fish size.

The positive relationship between heavy metal levels and fish size was attributed to the variations in feeding habits at different stage of fish life (Monikh et al. 2013). In addition, high concentrations of heavy metals in the surrounding water could result in continued metal accumulation in fish and increase of metal concentrations with fish size (Yi and Zhang 2012).

Human risk assessment

As shown in Table 2, all the median concentrations of Cd, Cu, Zn, Pb in the muscles of 14 fish species from Hainan were far below the maximum levels permitted for fish by China's Ministry of Health (MOH) (2012) and the European Commission (EC) (2006). However, approximately 50 % of fish species had Cr and inorganic As levels in excess of the permitted maximum level of 2 mg/kg (Cr) and 0.1 mg/kg [average concentration of inorganic As was estimated as 10 % of total As (USFDA 1993)] for fish products recommended by MOH (MOH 2012).

Due to their toxicity and threat to human health, different methods have been established to assess the potential risk of heavy metals to consumers (Yi et al. 2011; Tapia et al. 2012). In this study, both EDI and HQ were used for the risk assessment of wild marine fish from SCS consumed by local adults (Table 5). The daily consumption rate of fish by Hainan people was assumed to be 84.4 g d^{-1} $person^{-1}$ (Yang et al. 2009). An average weight of 58.1 kg was assumed for an adult from Hainan based on the average weight for a Chinese adult (Gu et al. 2006). ADI values were calculated from the PTWI values set by JECFA (FAO/WHO 2010). C_{fish} values of different heavy metals in muscles were averaged.

As shown in Table 5, HQ values of heavy metals via fish consumption decreased in the order of Cr > As > Cu > Cd > Zn. Although the RfD value of Pb was not regulated, the ratio of EDI to ADI is less than 1, indicating

Table 5 Daily intakes of heavy metals through marine fish consumption in Hainan Island

Metal	Concentration ($\mu g\ g^{-1}$)	EDI ($\mu g\ kg^{-1}\ d^{-1}$)	ADI ($\mu g\ kg^{-1}\ d^{-1}$)	EDI/ADI	RfD ($\mu g\ kg^{-1}\ d^{-1}$)	HQ
Cr	2.20	3.20	2.17	1.47	3.00	1.07
Cu	0.35	0.51	500	0.001	40	0.01
Zn	2.86	4.15	1000	0.004	15,000	0.0003
Pb	0.03	0.04	3.57	0.01		
As[a]	0.22	0.32	2.10	0.15	0.30	1.07
Cd	0.003	0.004	1.00	0.004	1.00	0.004

EDI estimated daily intake, *ADI* acceptable daily intake, *RfD* reference dose of trace elements as established by the United States Environmental Protection Agency (USEPA) (2005), *HQ* Hazard quotient (HQ) = EDI/RfD, if the ratio is <1, there is no obvious risk

[a] Average concentration of inorganic arsenic was estimated by using a value of 10 % of total arsenic in accordance with the United States Food and Drug Administration (USFDA) (1993)

that the health risk associated with Pb exposure was insignificant. HQ values of Cu, Zn, and Cd were all less than 1. In fact, the exposure levels of these metals were smaller than those stipulated in the RfD guidelines, suggesting that the daily intake of Cu, Zn, and Cd in this study would not likely cause any deleterious effects on fish consumer. However, the HQ values of Cr and As were larger than 1, which indicated that Cr and As would likely pose health risks to fish consumer. Therefore, as far as Cr and As were concerned, limited consumption of wild marine fish from SCS need to be regulated. It suggested that daily intake of wild marine fish should be less than 79.2 g for local residents.

Conclusions

The levels of Cd, Cu, Zn, and Pb in fish muscle were found to be below the established safety limits for these metals according to MOH and EC, but concentrations of Cr and As were above the maximum levels permitted. Cu, Zn, Cd and Cr were preferentially accumulated in the liver and Pb was always higher in the gill than in the other tissues. Significant differences in heavy metal concentrations were noted among the different fish species and was attributed to differences in habitat and diet. Hazard quotient values showed that Cr and As could pose health risks to fish consumers. Therefore, with respect to Cr and As, limited consumption of marine fish is advised. Identification of the explicit sources of Cr and As in SCS are required and should be established.

Acknowledgments This study was supported by China Postdoctoral Science Foundation (No. 2012M510201), and National Natural Science Foundation of China (Nos. 41176090; 51378488), and Hundred Talents Program of Chinese Academy of Sciences to Dr. X.R. Xu. We also thank Dr. Chris C. Feng for his help in revising the manuscript.

Conflict of interest We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled, "Heavy metals in wild marine fish from South China Sea: Levels, tissue- and species-specific accumulation and potential risk to humans".

References

Bilandžić N, Đokić M, Sedak M (2011) Metal content determination in four fish species from the Adriatic Sea. Food Chem 124: 1005–1010

Burger J, Gaines KF, Shane Boring C, Stephens WL, Snodgrass J, Dixon C, McMahon M, Shukla S, Shukla T, Gochfeld M (2002) Metal levels in fish from the Savannah River: potential hazards to fish and other receptors. Environ Res 89:85–97

Canli M, Atli G (2003) The relationships between heavy metal (Cd, Cr, Cu, Fe, Pb, Zn) levels and the size of six Mediterranean fish species. Environ Pollut 121:129–136

Celik U, Oehlenschlager J (2007) High contents of cadmium, lead, zinc and copper in popular fishery products sold in Turkish supermarkets. Food Control 18:258–261

Cheung KC, Leung HM, Wong MH (2008) Metal concentrations of common freshwater and marine fish from the Pearl River Delta, South China. Arch Environ Contam Toxicol 54:705–715

Copat C, Bella F, Castaing M, Fallico R, Sciacca S, Ferrante M (2012) Heavy metals concentrations in fish from Sicily (Mediterranean Sea) and evaluation of possible health risks to consumers. Bull Environ Contam Toxicol 88:78–83

Costa OTF, Fernandez MN (2002) Chloride cell changes induced by nitrite exposure in an Amazonian fish species. In: Kennedy C, Kolok A, MacKinlay D (eds) Aquatic toxicology: mechanism and consequences. International Congress of Fish Biology, Canada

Dalman O, Demirak A, Balci A (2006) Determination of heavy metals (Cd, Pb) and trace elements (Cu, Zn) in sediments and fish of the Southeastern Aegean Sea (Turkey) by atomic absorption spectrometry. Food Chem 95:157–162

de Mora S, Fowler SW, Wyse E, Azemard S (2004) Distribution of heavy metals in marine bivalves, fish and coastal sediments in the Gulf and Gulf of Oman. Mar Pollut Bull 49:410–424

Ebrahimpour M, Pourkhabbaz A, Baramaki R, Babaei H, Rezaei M (2011) Bioaccumulation of heavy metals in freshwater fish species Anzali, Iran. Bull Environ Contam Toxicol 87:386–392

EC (2006) European Commission Regulation (EC) No 1881/2006 maximum levels for certain contaminants in foodstuffs, OJ, L364/5

FAO (2012) Part 1: World review of fisheries and aquaculture. The state of world fisheries and aquaculture

FAO (2013) Fishery and aquaculture country profiles: China

FAO/WHO (2010) Evaluations of the Joint FAO/WHO Expert Committee on Food Additives (JECFA). International programme on chemical safety

Gu DF, He J, Duan XF, Reynolds K, Wu X, Chen J, Whelton PK (2006) Body weight and mortality among men and women in China. J Am Med Assoc 295:776–783

Hillwalker WE, Jepson PC, Anderson KA (2006) Selenium accumulation patterns in lotic and lentic aquatic systems. Sci Total Environ 366:367–379

Ip CCM, Li XD, Zhang G, Wong CSC, Zhang WL (2005) Heavy metal and Pb isotopic compositions of aquatic organisms in the Pearl River Estuary, South China. Environ Pollut 138:494–504

Liu JL, Xu XR, Yu S, Cheng HF, Hong YG, Feng XB (2014a) Mercury pollution in fish from South China Sea: Levels, species-specific accumulation, and possible sources. Environ Res 131:160–164

Liu JL, Wu H, Feng JX, Li ZJ, Lin GH (2014b) Heavy metal contamination and ecological risk assessments in the sediments and zoo benthos of selected mangrove ecosystems, South China. Catena 119:136–142

MOH (2012) China's Ministry of Health. Maximum levels of contaminants in seafood. GB2762-2012

Monikh FA, Safahieh A, Savari A, Ronagh MT, Doraghi A (2013) The relationship between Heavy metal (Cd Co, Cu, Ni and Pb) levels and the size of benthic, benthopelagic and pelagic fish species, Persian Gulf. Bull Environ Contam Toxicol 90:691–696

NBO (2012) National Bureau of Oceanography of China. Bulletin of Marine Environmental Quality

Pan K, Wang WX (2012) Trace metal contamination in estuarine and coastal environments in China. Sci Total Environ 421–422:3–16

Pintaeva ET, Bazarsadueva SV, Pertov EA, Smirnova OG (2011) Content and character of metal accumulation in fish of the

Kichera River (a tributary of Lake of Baikal). Contemp Probl Ecol 4:64–68

Ptashynski MD, Pedlar RM, Evans RE, Baron CL, Klaverkamp JF (2002) Toxicology of dietary nickel in lake whitefish (*Coregonus clupeaformis*). Aquat Toxicol 58:229–247

Qiu YW, Yu KF, Zhang G, Wang WX (2011) Accumulation and partitioning of seven trace metals in mangroves and sediment cores from three estuarine wetlands of Hainan Island, China. J Hazard Mater 190:631–638

Rahman MS, Molla AH, Saha N, Rahman A (2012) Study on heavy metals levels and its risk assessment in some edible fishes from Bangshi River, Savar, Dhaka, Bangladesh. Food Chem 134:1847–1854

Tapia J, Vargas-Chacoff L, Bertran C, Pena-Cortes F, Hauenstein E, Schlatter R, Jimenez C, Tapia C (2012) Heavy metals in the liver and muscle of Micropogonias manni fish from Budi Lake, Araucania Region, Chile: potential risk for humans. Environ Monit Assess 184:3141–3151

Türkmen M, Türkmen A, Tepe Y, Töre Y, Ateş A (2009) Determination of metals in fish species from Aegean and Mediterranean seas. Food Chem 113:233–237

Tuzen M (2003) Determination of heavy metals in fish samples of the middle Black Sea (Turkey) by graphite furnace atomic absorption spectrometry. Food Chem 80:119–123

USEPA (2005) Risk-based concentration table, 2005. Region 3, Philadelphia

USFDA (1993) Guidance document for arsenic in shellfish center for food safety and applied nutrition. Washington, DC

Uysal K, Köse E, Bülbül M, Dönmez M, Erdogan Y, Koyun M, Ömeroglu Ç, Özmal F (2009) The comparison of heavy metal accumulation ratios of some fish species in Enne Dame Lake (Kutahya/Turkey). Environ Monit Assess 157:355–362

Vane CH, Harrison I, Kim AW, Moss-Hayes V, Vikers BP, Hong K (2009) Organic and metal contamination in surface mangrove sediments of South China. Mar Pollut Bull 58:134–144

Vaseem H, Banerjee TK (2013) Contamination of metals in different tissues of Rohu (Labeo rohita, Cyprinidae) collected from the Indian River Ganga. Bull Environ Contam Toxicol 91:36–41

Wang WX, Rainbow PS (2008) Comparative approaches to understand metal bioaccumulation in aquatic animals. Comp Biochem Physiol: Part C 148:315–323

Wang SL, Xu XR, Sun YX, Liu JL, Li HB (2013) Heavy metal pollution in coastal areas of South China: A review. Mar Pollut Bull 76:7–15

Widianarko B, Van Gestel CAM, Verwejj RA, Van Straalen NM (2000) Associations between trace metals in sediment, water, and guppy, *Poecilia reticulate* (Peters), from urban streams of Semarang, Indonesia. Ecotoxicol Environ Saf 46:101–107

Xia N, Xue G, Fu Y, Yang Y, Liu C, Ma R (2011) Analysis of ecological risk and the content situation of heavy metals in surface sediments of Hainan Island's inshore. Resour Environ Eng 25:244–247 (in Chinese)

Yang B, Pan XH, Li YZ, Chen YQ, Zhai FY (2009) Survey of dietary patterns and nutrients intake status of residents in Hainan. China Trop Med 9:1673–1692 (in Chinese)

Yi YJ, Zhang SH (2012) Heavy metal (Cd, Cr, Cu, Hg, Pb, Zn) concentrations in seven fish species in relation to fish size and location along the Yangtze River. Environ Sci Pollut Res 19:3989–3996

Yi Y, Yang Z, Zhang S (2011) Ecological risk assessment of heavy metals in sediment and human health risk assessment of heavy metals in fishes in the middle and lower reaches of the Yangtze River basin. Environ Pollut 159:2575–2585

Zhang L, Wang WX (2007) Size-dependence of the potential for metal biomagnification in early life stages of marine fish. Environ Toxicol Chem 26:787–794

Zhang W, Wang WX (2012) Large-scale spatial and interspecies differences in trace elements and stable isotopes in marine wild fish from Chinese waters. J Hazard Mater 215–216:65–74

Zhao S, Feng C, Quan W, Chen X, Niu J, Shen Z (2012) Role of living environments in the accumulation characteristics of heavy metals in fishes and crabs in the Yangtze River Estuary, China. Mar Pollut Bull 64:1163–1171