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Large-scale spatial and interspecies differences in trace elements and stable isotopes in marine wild fish from Chinese waters

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ABSTRACT

We conducted a large scale investigation of twelve trace element levels and stable isotopes ($\delta^{13}C$ and $\delta^{15}N$) in twenty-nine marine wild fish species collected from Chinese coastal waters. Trace element levels varied significantly with species. Clear spatial variations were found for Al, As, Cd, Cr, Fe, Ni, and Pb, whereas Ag, Cu, Mo, Se and Zn did not show much spatial variation. The Pearl River Estuary contained the highest concentrations of Al, Cr, Ni, and Pb, whereas the most southern waters (Haikou) contained the lowest concentrations of Al, Fe, and Pb. There was no correlation between log-transformed trace elements concentrations and $\delta^{15}N$ values or $\delta^{13}C$ values, indicating no biomagnification among these trace elements. The calculated hazard quotients (HQ) of 10 elements were less than 1, thus there was no obvious health risk from the intake of trace elements through marine wild fish consumption.

1. Introduction

With the recent very rapid development of industry and agriculture in China, a large number of harmful substances have been discharged into the sea, resulting in coastal water pollution. These substances are often persistent and have potentials of being bioaccumulated by the marine organisms. In a most recent review of trace metal pollution in estuarine and coastal waters of China, Pan and Wang [1] concluded that industrial and domestic sewage discharges, mining, smelting, and *e*-wastes recycling are the important sources contributing to coastal pollution in China. Metal contamination in the coastal environments is closely associated with accelerated economic growth in the past decades. Various compartments such as sediments, water and organisms collected from the heavily industrialized areas often contained alarmingly high metal concentrations. Such elevated levels of metal contamination along China's coastal environment can increase the risk of metal exposure to humans by seafood consumption.

Fish are the major seafoods consumed by humans. FAO [2] estimated that about 75% (105.6 million tons) of worldwide fish production were directly consumed by human in 2004 alone. In the China Seas, there are a variety of marine species and outputs, but all of these marine fish species are currently under serious threats. Levels of contaminants in fish are of particular interests due to their potential risks to humans. Numerous studies have measured the trace elements levels in different species of edible fish worldwide [3–7]. Several earlier studies in China reported trace elements contamination in seawater, sediments, and bivalves [1], with only few focusing on marine fish [8–10].

This study represents the first large-scale investigation of multi-elemental accumulation in marine wild fish from China Seas. We targeted the analysis of twelve trace elements (Ag, Al, As, Cd, Cr, Cu, Fe, Mo, Ni, Pb, Se, and Zn) in their muscle tissues. Mercury was not specifically analyzed in this study, despite the fact that it is probably the most important in terms of human health exposure assessment. The marine wild fish were caught from seven main coastal areas from Northern to Southern parts of China. We also collected the marine wild fish from the Pearl River Estuary, the second largest estuary in China. With the establishment of many industrial developmental zones along the coastal cities, estuaries are especially vulnerable to metal pollution due to uncontrolled release of industrial effluents. The main objectives of this study were to examine whether the marine wild fish were contaminated with trace elements, and to test whether there were any spatial or interspecific variations in the coastal or estuarine environment. Health risk assessment was then conducted to evaluate whether these marine wild fish presented any potential risk to humans as a result of consumption. From a public health perspective, this study could provide consumers with better knowledge of contamination problems associated with seafood consumption. In addition, we also used the stable isotope approach ($\delta^{13}C$ and $\delta^{15}N$) to estimate

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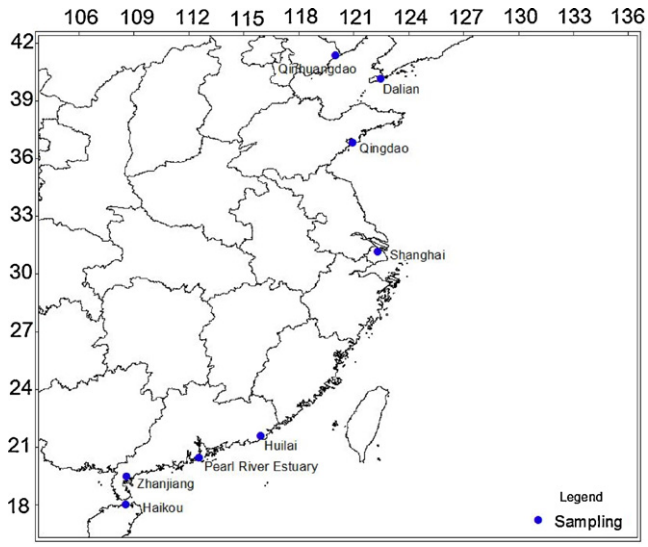

Fig. 1. Sampling stations in coastal waters of China.

the relationships among concentrations of trace elements, food sources and trophic levels of fish species.

2. Materials and methods

2.1. Sampling

Twenty-nine marine wild fish species of similar sizes were collected from eight stations along the coastal areas in China, including seven main coastal cities (Qinhuangdao, Dalian, Qingdao, Shanghai, Huilai, Zhanjiang and Haikou) and the Pearl River Estuary (Fig. 1), between April and May 2010. Each species were represented by 10–20 individuals, with a body length of approximately 10 cm. The collected samples were transferred to the laboratory and rinsed with distilled water three times. The dorsal muscles of the fishes were then dissected and stored in plastic bags at −20 °C. The wet weights of all fish muscle tissues were first recorded, and the tissues were then freezed dried until constant weight, after which their dry weights were recorded. Dried samples were homogenized and stored in small polyethylene plastic bags until analysis.

2.2. Chemical analysis

About 0.2–0.3 g of samples were weighed in 15 ml volumetric flasks and digested with 3 ml of concentrated HNO_3 (65%) in heating block at 80 °C for 24 h till clarification. After cooling, the samples were diluted to 10 ml with double deionized water (Milli-Q Millipore 18.2 M cm^{-1} resistivity). A blank digest was carried out in the same way. The samples were analyzed for twelve trace elements: Ag, Al, As, Cd, Cr, Cu, Fe, Mo, Ni, Pb, Se, and Zn, using inductively coupled plasma mass spectrometer (ICP-MS). The standard solution was prepared from a stock solution (China National Standard, National Institute of Metrology, China).

The accuracy of our digestion method was verified by analysis of standard reference material of 2976 mussel tissue (National Institute of Standards and Technology, the National Research Council Canada, and the International Atomic Energy Agency, Marine Environment Laboratory, Monaco). All samples were blank-subtracted. Limit of detection (LOD) was defined as three times the signal-to-noise ratio for the analyzed matrix or blank value for each sample. The method detection limit (MDL) was defined either as three times the standard deviation of the blank samples or, if the blanks had no detectable contamination, as the instrumental detection limit (IDL). IDL values were all lower than 0.1 ng/L. The recovery rate was Ag 97.3%, Al 85.5%, As 101.8%, Cd 108.9%, Cr 101.7%, Cu 100.3%, Fe 100.9%, Ni 108.7%, Pb 89.8%, Se 119.7%, and Zn 91.9%, respectively. Because there was no Mo standard reference, the recovery rate of Mo was not determined. Concentrations of Al, As, Cu, Fe, Se, and Zn were expressed as μg/g dry weight, and those of Ag, Cd, Cr, Mo, Ni, and Pb were expressed as ng/g dry weight.

2.3. Stable isotope analysis

Homogenized dry fish samples were weighed in tin capsules for analyses of $\delta^{15}N$ and $\delta^{13}C$. Stable isotope ratios of carbon and nitrogen were analyzed using an Isotope Ratio Mass Spectrometer and Elemental Analyzer (Thermo Fisher Scientific, Inc., USA). Ratios were compared to standard gases Pee Dee Belemnite for $\delta^{13}C$ and atmospheric nitrogen (AIR) for $\delta^{15}N$. Values for $\delta^{13}C$ and $\delta^{15}N$ were calculated and reported using the standard delta (δ) notation in parts per thousand (‰) as follows:

$$\delta X = \left[\left(\frac{R_{\text{sample}}}{R_{\text{standard}}}\right) - 1\right] \times 1000 \quad (1)$$

where X is $\delta^{13}C$ or $\delta^{15}N$ and R is the corresponding ratio $\delta^{13}C/^{12}C$ or $\delta^{15}N/^{14}N$. The R_{standard} values were based on Pee Dee Belemnite for $\delta^{13}C$ and atmospheric nitrogen (N_2) for $\delta^{15}N$.

2.4. Human exposure assessment

The human risk assessment for Chinese people was conducted using the provisional tolerance weekly intake (PTWI), acceptable daily intake (ADI), and reference dose (RfD) previously established by the United States Environmental Protection Agency [11] and the Joint FAO/WHO Expert Committee on Food Additives (JECFA) (Joint Food and Agriculture Organization/World Health Organization Expert Committee on Food Additives) [12]. The estimated daily intake (EDI) (μg/kg/day) was calculated using the following equation:

$$\text{EDI} = C_{\text{fish}} \times \left[\frac{dc_{\text{fish}}}{bw}\right] \quad (2)$$

where C_{fish} = average trace elements concentration in fish muscle (μg/g wet weight), dc_{fish} = daily fish consumption (g/day) per capita as recorded by the FAO (2008) [13], and bw = the average body weight (kg) of the target population. The hazard quotient (HQ) was calculated by dividing the EDI, by the established RfD to assess the health risk from fish consumption. There would be no obvious risk if the HQ were less than 1.

2.5. Statistical analysis

Statistical analyses were executed by the programs SPSS version 13.0 for windows. A one-way analysis of variance (ANOVA) followed by a least significant difference (LSD) test was used to verify any statistically significant difference ($p < 0.05$) among fish species in the same location. Linear regression was used to assess the correlation between trace elements concentrations and $\delta^{15}N$. Trace elements concentrations were logarithmically transformed (base 10). Relationship was considered statistically significant at $p < 0.05$.

3. Results

3.1. Geographic variation of metal concentrations

The concentrations of 12 trace elements in fish collected along the Chinese coastal waters are shown in Table 1 . Differences of trace elements concentrations in different fish and from different locations are described below.

The Ag concentrations in the fish were generally very low (0.38–7.52 ng/g) among all the locations. Several species of fish had their tissue Ag concentrations lower than the limit of quantitation (LOQ) or method detection limit (MDL) (0.1 ng/L). There was no clear spatial difference among all the areas. The highest Ag concentration was found in *Clupanodon thrissa* (7.52 ng/g) from the Pearl River Estuary. The Al concentrations in the fish ranged from 1.19 to 47.6 μg/g among all the locations. The Pearl River Estuary showed the highest Al levels (18.0–47.6 μg/g), which were about 5–9 times higher than the lowest Al levels (2.54–8.97 μg/g) from Haikou. No clear spatial difference was found among the other areas, except that *Cynoglossus joyneri* from Qinhuangdao had an Al concentration of 37.0 μg/g compared to 22.3 μg/g from Shanghai.

The As concentrations in different fish species had a wide range of variation (2.09–134 μg/g) and showed a strong difference among the different locations. Huilai and Zhanjiang had relatively higher As concentrations (ranging from 17.9 to 36.1 μg/g, and from 4.81 to 134 μg/g, respectively). The highest concentration was recorded for *Trypauchen vagina* from Zhanjiang (134 μg/g), followed by *Cynoglossus joyneri* from Qinhuangdao (48.4 μg/g). No spatial variance was detected among the other areas, with a few exceptions (e.g., *Gerreomorpha japonica* from Zhanjiang had an As concentration of 38.9 μg/g, and *Sillago japonica* from Haikou had an As concentration of 24.8 μg/g).

The Cd concentrations in different fish species from different stations ranged from 2.37 to 71.3 ng/g. Interestingly, Cd concentrations in the fish muscles from the northern sites were generally higher than those from the southern sites. For example, the Cd concentrations in Qinhuangdao (9.68–59.9 ng/g), Dalian (19.4–42.0 ng/g), Qingdao (17.0–30.5 ng/g) were higher than those in Huilai (4.09–6.75 ng/g), Pearl River Estuary (2.54–29.6 ng/g), Zhanjiang (2.37–8.35 ng/g), and Haikou (2.43–21.3 ng/g), with a few exceptions noted. The Cr concentrations ranged from 17.6 to 121 ng/g among all the locations. The highest Cr concentrations (71.3–109 ng/g) were detected in the Pearl River Estuary, and fish from Zhanjiang generally contained lower Cr levels (17.6–45.4 ng/g), except *Sillago japonica* (87.0 ng/g). Other areas had comparable Cr levels, except *Cynoglossus joyneri* from Qinhuangdao (121 ng/g).

The Cu concentrations in the fish muscles ranged from 0.34 to 7.35 μg/g among all the locations. No significant difference was found among all the areas, with a few exceptions. Interestingly, *Clupanodon thrissa* collected from three stations had the highest Cu muscle concentrations (5.88 μg/g in Qinhuangdao, 5.72 μg/g in Qingdao, and 7.35 μg/g in Pearl River Estuary). *Ilisha elongata* from Qingdao also had high Cu tissue concentration (5.78 μg/g). The Fe concentrations in the fish ranged from 474 to 11788 μg/g among all the locations. Fe levels in Haikou were the lowest (550–1983 μg/g), whereas there was no clear geographic difference among the other areas. Fe concentrations in *Trypauchen vagina* (11788 μg/g from Pearl River Estuary, 9937 μg/g from Zhanjiang) were both the highest among the same fish species collected from the different locations.

The Mo concentrations in the fish ranged from 8.75 to 81.4 ng/g among all the locations. No clear variation of Mo concentrations was detected, apart from *Chaeturichthys stigmatias* (81.4 ng/g) in the Pearl River Estuary. The Ni concentrations in the fish ranged from 22.3 to 461 ng/g among all the locations. The Pearl River Estuary had the highest Ni concentrations (126–461 ng/g). There was no clear difference among the other areas, although *Scorpaena neglecta* collected from the 3 stations differed by 2.6–5.6 fold (123 ng/g, 46.2 ng/g, and 22.3 ng/g from Qinhuangdao, Shanghai, and Zhanjiang, respectively).

The Pb concentrations in the fish ranged from 2.69 (Haikou) to 290 (Qinhuangdao) ng/g among all the locations. In Pearl River Estuary, the concentrations of Pb were also comparatively high (54.2–128 ng/g), whereas lower Pb levels (2.69–51.2 ng/g) were found in Haikou. Other stations had a rather comparable Pb level in the fish tissues, except that *Cynoglossus joyneri* in Qinhuangdao showed the highest Pb levels (290 ng/g). There was no significant variation of Se in the fish muscles (1.84–7.41 μg/g) among all the locations. At the same time, the Zn concentrations (10.4–79.1 μg/g) did not show clear geographic differences, with the exception of *Hemirhamphus sajori* (79.0 μg/g) from Qinhuangdao, and *Harpodon nehereus* (79.1 μg/g) from Shanghai.

3.2. Differences of metal concentrations among different fish species

In general, Fe had the highest tissue concentrations, followed by Zn, Al, As, Se, Cu, Cd, Cr, Mo, Ni, and Pb, while the Ag levels were the lowest, among different locations and fish species. The sequence was somewhat different among the different locations.

In Qinhuangdao, *Cynoglossus joyneri* showed the highest Al, As, Cr, Fe, Ni, and Pb levels. *Hemirhamphus sajori* had the highest Ag and Zn levels, and *Clupanodon thrissa* had the highest Cu concentration. In Dalian, the maximum concentrations of Ag, As, Cd, Cu, Fe, Mo, Pb, Se, and Zn were noted in *Pseudosciaena crocea*, and the lowest concentrations of all trace elements were found in *Argyrosomus aneus*.

In Qingdao, *Ilisha elongate* showed the highest concentrations of Cu, Fe, Se, and Zn, and *Clupanodon thrissa* had the highest levels of Ag, Cr, Mo, and Pb; *Johnius belengerii* had the highest levels of Al (17.2 μg/g) and Ni (153 ng/g); *Scorpaena neglecta* had the highest levels of As. Cd appeared no difference in all the fish species. In Shanghai, *Harpodon nehereus* showed the highest levels of Cd, Cu, Mo, Ni, Pb, and Zn, and *Cynoglossus joyneri* had the highest levels of Al, As, Cr, and Fe. *Pampus argenteus* and *Scorpaena neglecta* showed comparatively lower trace elements concentrations.

In Pearl River Estuary, *Trypauchen vagina* had the highest levels of As, Fe, Pb, and Se, and *Chaeturichthys stigmatias* had the highest levels of Cd, Mo, and Ni. *Clupanodon thrissa* had the highest levels of Ag and Cu, and *Leiognathus bindus* had the highest levels of Zn. *Johnius belengerii* and *Polynemus sextarius* showed relatively lower trace elements concentrations as compared with other fish species.

In Zhanjiang, *Trypauchen vagina* showed the highest levels of As, Fe, Se, and Zn, and *Solea ovata* had the highest levels of Al, Mo, Ni, and Pb. The As concentration in *Trypauchen vagina* reached 134 μg/g, the highest concentration measured in this study. In Haikou, *Upeneus sulphureus* had the highest levels of Ag, Al, Ni, and Pb, and *Sillago japonica* had the highest levels of As and Zn. *Atrobucca nibe* had the highest levels of Cu and *Psenopsis anomala* had the highest levels of Cd.

3.3. Stable isotopes analysis

The stable isotope $\delta^{13}C$ and $\delta^{15}N$ signatures in marine fish are also shown in Table 1. The $\delta^{13}C$ values varied over a range of −22.69‰ to −14.15‰, and the $\delta^{15}N$ values ranged from 7.77‰ to 15.86‰. The Pearl River Estuary had significantly different $\delta^{13}C$ signatures compared with Dalian, Qingdao, and Haikou. Haikou had significant difference in $\delta^{13}C$ compared with other locations, except Dalian, and Qingdao. Shanghai had significant different $\delta^{15}N$ values

Table 1
Trace element concentrations (dry weight basis) and $\delta^{13}C$ and $\delta^{15}N$ values in marine wild fish species collected from different locations of Chinese coastal waters. Data are mean ± SD (n = 10–20). For each trace element, different letters indicate significant differences between fish species in the same location ($p < 0.05$). n.d (not detectable).

Locations	Species	Number	Different trace element concentrations												$\delta^{13}C$(‰)	$\delta^{15}N$(‰)
			Ag (ng/g)	Al (μg/g)	As (μg/g)	Cd (ng/g)	Cr (ng/g)	Cu (μg/g)	Fe (μg/g)	Mo (ng/g)	Ni (ng/g)	Pb (ng/g)	Se (μg/g)	Zn (μg/g)		
Qinhuangdao	*Clupanodon thrissa*	19	0.64±0.27^{a}	11.1±4.79^{a}	8.24±2.55^{bc}	23.7±8.43^{a}	50.0±9.62^{a}	5.88±1.18^{c}	4185.1±554.1^{c}	13.7±3.07^{ab}	56.9±9.46^{a}	40.0±33.4^{a}	4.70±1.48^{c}	50.5±13.1^{b}	–16.13	12.73
	Cynoglossus joyneri	10	2.87±1.15^{b}	37.0±14.6^{b}	48.4±6.32^{d}	21.2±4.92^{a}	121±41.4^{b}	1.52±0.18^{a}	6476.6±2767.5^{d}	22.9±10.8^{bc}	149±40.0^{c}	290±134^{b}	3.51±0.48^{a}	21.6±3.90^{a}	–15.51	12.4
	Glossogobius giuris	10	3.88±0.83^{c}	13.3±6.81^{a}	4.00±0.42^{a}	50.9±16.8^{b}	64.9±16.4^{a}	2.29±0.37^{b}	3570.6±1016.0^{bc}	33.8±6.30^{c}	113±14.1^{b}	49.5±19.3^{a}	4.29±0.38^{abc}	48.9±6.60^{b}	–18.00	14.08
	Hemirhamphus sajori	10	5.95±1.33^{d}	6.46±0.57^{a}	5.10±0.35^{abc}	20.2±2.91^{a}	67.8±47.9^{a}	1.47±0.38^{a}	1421.0±183.7^{ab}	31.6±9.29^{c}	62.5±7.62^{a}	18.3±6.09^{a}	4.42±0.63^{bc}	79.0±8.29^{c}	–18.72	10.87
	Lateolabrax japonicus	10	n.d.	5.68±0.38^{a}	8.75±2.89^{c}	12.7±6.63^{a}	48.3±3.54^{a}	1.52±0.26^{a}	1448.4±232.4^{ab}	19.6±4.40^{ab}	39.8±4.39^{a}	14.6±3.80^{a}	4.94±0.73^{c}	43.6±4.85^{b}	–16.88	14.72
	Platycephalus indicus	20	n.d.	6.57±1.34^{a}	6.87±1.92^{abc}	9.68±3.15^{a}	48.8±2.25^{a}	1.43±0.37^{a}	1328.9±266.0^{a}	8.75±1.38^{a}	53.9±13.4^{a}	10.9±8.52^{a}	3.42±0.48^{a}	21.9±0.98^{a}	–17.23	12.73
	Scorpaena neglecta	10	2.90±1.54^{b}	8.04±2.17^{a}	4.60±0.45^{ab}	59.9±33.9^{b}	66.8±32.4^{a}	1.46±0.16^{a}	2089.6±588.0^{abc}	19.4±6.96^{ab}	123±13.1^{b}	35.4±11.2^{a}	3.80±0.49^{ab}	27.5±2.65^{a}	–15.63	13.03
Dalian	*Argyrosomus aneus*	20	0.54±0.20^{a}	8.35±1.27^{a}	3.86±0.37^{b}	19.4±6.07^{a}	58.1±14.2^{a}	1.00±0.10^{a}	1472.4±407.6^{a}	10.8±3.53^{a}	43.7±5.99^{a}	9.65±3.78^{a}	2.14±0.16^{a}	18.4±2.31^{a}	–21.51	10.96
	Pseudosciaena crocea	20	3.11±1.19^{b}	7.79±1.29^{a}	7.04±0.43^{c}	42.0±7.10^{b}	55.9±5.92^{a}	2.87±0.26^{b}	2570.9±413.9^{b}	16.6±5.43^{a}	64.9±8.96^{b}	46.4±22.3^{c}	4.41±0.50^{c}	24.6±2.04^{b}	–17.81	12.17
	Sillago japonica	20	0.40±0.14^{a}	10.6±2.60^{b}	3.41±0.87^{a}	37.7±13.6^{b}	81.7±39.8^{b}	1.04±0.23^{a}	1741.9±547.6^{a}	11.2±1.92^{a}	75.8±27.3^{c}	28.4±19.7^{b}	2.95±1.19^{b}	23.6±5.39^{b}	–15.84	13.33
Qingdao	*Clupanodon thrissa*	20	1.44±0.48^{b}	9.16±3.39^{a}	6.72±1.13^{a}	24.0±9.79^{a}	74.4±25.3^{b}	5.72±1.03^{c}	6122.2±1054.5^{c}	34.1±15.2^{b}	77.1±31.2^{b}	90.2±39.1^{c}	3.86±0.98^{a}	41.1±8.62^{b}	–17.75	10.96
	Ilisha elongata	20	0.55±0.16^{a}	10.5±1.59^{a}	13.9±3.11^{c}	20.0±8.70^{a}	59.3±12.4^{a}	5.78±1.55^{c}	6329.3±1050.8^{c}	16.3±3.63^{a}	67.5±26.8^{b}	16.0±6.48^{ab}	6.99±1.25^{c}	41.8±8.99^{b}	–17.17	10.34
	Johnius belengerii	20	0.77±0.32^{a}	17.2±3.61^{b}	10.4±3.30^{b}	30.5±10.5^{a}	65.3±6.88^{ab}	2.15±0.27^{b}	2508.8±393.1^{b}	19.5±8.02^{a}	152.5±40.2^{c}	26.4±18.6^{b}	5.55±0.73^{b}	27.2±4.68^{a}	–17.34	9.75
	Scorpaena neglecta	20	0.69±0.43^{a}	9.02±1.27^{a}	14.3±3.46^{c}	17.0±7.34^{a}	62.2±22.3^{a}	1.15±0.25^{a}	1032.9±274.8^{a}	14.1±4.53^{a}	46.1±9.48^{a}	5.43±4.41^{a}	6.04±0.69^{b}	31.1±4.84^{a}	–18.48	13.26
Shanghai	*Collichthys lucidus*	20	0.41±0.16^{a}	14.0±4.49^{bc}	6.06±3.28^{c}	12.4±5.48^{ab}	87.4±16.4^{b}	1.26±0.25^{c}	2401.6±671.8^{c}	19.1±5.47^{ab}	81.0±18.5^{b}	31.3±14.8^{bc}	3.47±0.67^{d}	25.0±5.50^{b}	–16.84	7.77
	Cynoglossus joyneri	13	n.d.	22.3±5.27^{d}	17.6±2.23^{d}	15.0±6.37^{b}	89.9±35.6^{b}	1.15±0.18^{c}	2609.4±542.5^{c}	18.7±9.76^{ab}	96.0±16.4^{c}	43.5±16.3^{cd}	3.08±0.39^{c}	18.5±1.87^{a}	–19.82	11.71
	Harpodon nehereus	20	5.47±1.34^{b}	16.7±8.09^{c}	2.09±0.28^{a}	71.3±20.9^{c}	80.7±22.0^{b}	1.27±0.19^{c}	2323.7±605.9^{c}	35.4±12.0^{c}	141±27.5^{d}	53.3±36.9^{d}	1.84±0.27^{a}	79.1±12.8^{c}	–17.05	8.99
	Pampus argenteus	20	n.d.	11.1±2.91^{b}	6.59±2.49^{c}	11.1±5.41^{ab}	59.6±10.2^{a}	0.97±0.34^{b}	1478.4±402.5^{b}	13.3±4.08^{a}	36.0±17.5^{a}	15.6±11.3^{ab}	1.98±0.42^{a}	21.9±3.01^{ab}	–15.81	11.14
	Scorpaena neglecta	20	n.d.	6.19±0.68^{a}	4.43±0.91^{b}	5.49±1.78^{a}	55.1±10.5^{a}	0.76±0.09^{a}	797.0±249.2^{a}	21.0±10.8^{b}	46.2±10.3^{a}	12.5±8.55^{a}	2.44±0.32^{b}	23.0±2.69^{ab}	–15.39	8.52
Huilai	*Johnius belengeriii*	11	0.67±0.30^{a}	11.1±3.54^{b}	17.9±8.01^{a}	4.09±1.03^{a}	56.0±9.15^{a}	1.29±0.22^{b}	2962.6±1053.6^{b}	12.6±7.76^{a}	92.3±16.5^{b}	70.0±29.6^{b}	2.91±0.30^{a}	18.7±1.42^{b}	–16.33	12.42
	Sillago japonica	16	0.74±0.30^{a}	6.87±0.86^{a}	36.1±12.3^{b}	6.75±2.63^{b}	50.4±18.1^{a}	0.82±0.11^{a}	849.4±224.5^{a}	9.69±2.59^{a}	62.9±8.20^{a}	29.0±15.4^{a}	3.66±1.07^{a}	16.4±3.12^{a}	–16.63	12.44
Pearl River Estuary	*Chaeturichthys stigmatias*	20	3.30±1.59^{c}	33.6±13.6^{cd}	3.88±0.42^{ab}	29.6±15.2^{d}	105±36.7^{b}	2.15±0.88^{cd}	5325.5±2379.5^{bc}	81.4±38.3^{d}	461±121^{d}	111±42.2^{c}	3.80±0.45^{b}	23.5±2.46^{ab}	–19.25	13.96
	Clupanodon thrissa	18	7.52±2.32^{d}	29.9±12.4^{bc}	3.60±0.53^{ab}	26.8±15.1^{d}	101±30.2^{ab}	7.35±1.85^{f}	6493.5±2009.1^{c}	47.6±20.2^{c}	262±93.0^{b}	113±44.9^{c}	3.54±0.52^{ab}	42.9±7.54^{c}	–22.69	10.44
	Coilia mystus	20	2.04±1.00^{b}	41.1±15.3^{de}	4.24±0.89^{ab}	24.3±13.4^{d}	109±32.3^{b}	1.55±0.38^{ab}	4447.4±1432.5^{ab}	19.5±6.20^{a}	257±107^{b}	99.5±40.0^{bc}	3.34±0.71^{ab}	24.3±7.20^{ab}	–17.72	14.1
	Johnius belengerii	10	0.50±0.21^{a}	24.9±7.66^{abc}	5.19±4.57^{abc}	5.75±3.12^{ab}	93.7±35.9^{ab}	1.16±0.15^{a}	3441.4±978.3^{a}	10.8±3.86^{a}	138±32.4^{a}	66.4±26.7^{ab}	4.78±1.18^{c}	23.9±4.81^{ab}	–22.52	20.18

Table 1
(Continued).

	Leiognathus bindus	17	0.94±0.44^{a}	25.6±7.58^{abc}	5.55±1.17^{bc}	3.77±2.67^{a}	82.3±26.1^{ab}	1.76±0.33^{bc}	3760.8±1124.1^{ab}	43.0±16.9^{bc}	146±47.0^{a}	54.2±43.0^{a}	2.86±0.45^{a}	52.3±14.7^{d}	–21.41	12.6
	Oateomugil ophuyseni	10	0.99±0.43^{a}	19.4±5.16^{a}	7.78±1.27^{c}	12.6±3.96^{bc}	71.3±9.95^{a}	3.46±0.92^{e}	5357.4±1332.6^{bc}	12.9±5.05^{a}	185±39.9^{a}	100±30.9^{bc}	3.66±0.74^{ab}	29.1±4.85^{b}	–18.3	12.89
	Platycephalus indicus	11	0.62±0.25^{a}	47.6±17.0^{c}	2.69±0.83^{a}	2.54±0.82^{a}	108±44.1^{b}	1.09±0.28^{a}	5138.5±1747.6^{bc}	18.3±6.97^{a}	126±43.4^{a}	101±66.1^{bc}	3.94±0.48^{b}	27.0±3.97^{b}	–18.55	13.73
	Polynemus sextarius	11	3.20±1.75^{c}	23.9±6.60^{ab}	7.73±1.04^{c}	6.23±4.35^{ab}	92.8±60.2^{ab}	2.45±0.55^{d}	4360.8±1066.0^{ab}	20.9±5.40^{a}	173±50.4^{a}	70.5±50.8^{ab}	3.46±0.88^{ab}	19.6±2.64^{a}	–16.51	14.65
	Trypauchen vagina	20	1.12±0.41^{a}	18.0±6.20^{a}	14.8±5.50^{d}	15.7±6.05^{c}	85.8±17.0^{ab}	1.10±0.12^{a}	11788.3±2576.7^{d}	34.2±19.0^{b}	370±79.2^{c}	128±47.2^{c}	7.41±1.74^{d}	40.9±4.16^{c}	–20.11	9.73
Zhanjiang	*Gerreomorpha japonica*	20	0.85±0.39^{a}	10.6±2.21^{bc}	38.9±15.5^{c}	8.35±3.08^{a}	17.6±5.62^{a}	0.95±0.20^{c}	1123.5±282.3^{a}	12.9±4.37^{a}	50.3±10.3^{b}	34.6±20.2^{c}	4.43±1.27^{c}	24.5±4.02^{cd}	–15.32	15.04
	Scorpaena neglecta	20	0.74±0.45^{a}	1.19±0.56^{a}	6.55±2.67^{a}	5.97±2.30^{a}	30.4±18.1^{ab}	0.34±0.04^{a}	473.6±126.2^{a}	9.27±6.39^{a}	22.3±5.51^{a}	6.91±3.50^{a}	2.71±0.33^{a}	10.4±0.91^{a}	–16.9	13.44
	Siganus fuscescens	20	2.20±1.45^{c}	8.03±2.51^{b}	4.81±0.70^{a}	54.1±44.9^{b}	17.8±4.81^{a}	1.94±0.49^{e}	2578.0±491.2^{b}	31.4±8.94^{c}	65.5±21.2^{b}	27.1±10.8^{bc}	3.79±1.01^{b}	27.3±3.95^{d}	–17.06	11.17
	Sillago japonica	20	1.02±0.$_{61}$ ^{ab}	11.2±2.80^{c}	21.3±7.07^{b}	46.5±31.7^{b}	87.0±37.9^{c}	1.65±0.36^{d}	2770.8±726.5^{b}	18.6±4.59^{b}	60.8±17.3^{b}	22.9±9.40^{bc}	4.73±0.68^{c}	19.4±2.80^{b}	–14.39	14.98
	Solea ovata	20	2.33±1.26^{c}	21.8±7.37^{c}	12.1±3.31^{ab}	5.83±1.78^{a}	38.6±18.8^{b}	1.48±0.37^{d}	3533.7±1238.1^{c}	38.7±11.5^{d}	125±34.8^{d}	119±40.7^{e}	3.73±0.93^{b}	23.1±2.86^{c}	–14.85	14.91
	Trypauchen vagina	17	1.51±0.73^{b}	8.96±3.02^{bc}	133.7±44.9^{d}	7.33±4.81^{a}	45.4±41.5^{b}	1.11±0.19^{c}	9936.8±2429.9^{d}	30.8±12.2^{c}	105±28.0^{c}	90.0±62.4^{d}	6.72±1.62^{d}	42.4±11.4^{e}	–14.15	15.86
	Zebrias zebra	20	0.70±0.42^{a}	19.1±5.37^{d}	39.3±7.76^{c}	2.37±0.67^{a}	32.0±17.7^{ab}	0.67±0.11^{b}	2187.4±740.3^{b}	23.8±9.94^{b}	64.3±24.5^{b}	42.3±15.1^{c}	2.18±0.31^{a}	16.9±1.31^{c}	–14.26	14.59
Haikou	*Atrobucca nibe*	20	n.d.	3.14±1.06^{a}	4.28±2.00^{a}	6.61±2.96^{a}	56.2±13.1^{a}	2.04±0.51^{e}	1982.9±514.5^{d}	12.5±4.59^{a}	26.7±5.0$_{4}$ ^{a}	6.94±6.33^{a}	4.04±0.61^{bc}	21.8±1.97^{b}	–16.19	12.79
	Lactarius lactarius	19	n.d.	3.72±1.87^{a}	3.43±0.68^{a}	3.78±1.84^{a}	87.3±44.5^{bc}	1.03±0.40^{b}	1019.3±224.8^{b}	15.9±6.56^{a}	66.4±23.9^{b}	2.69±2.66^{a}	4.48±0.41^{d}	20.0±2.65^{b}	–16.41	12.87
	Pampus argenteus	20	0.38±0.14^{a}	5.79±$_{2.52}$ ^{b}	11.1±1.51^{b}	15.8±4.62^{b}	98.2±49.6^{c}	0.43±0.07^{a}	1187.8±239.4^{b}	17.6±4.12^{a}	73.8±32.5^{b}	12.1±6.25^{a}	4.47±0.49^{d}	20.1±2.64^{b}	–16.92	11.97
	Psenopsis anomala	20	1.0±0.58^{a}	6.78±2.84^{b}	12.2±1.56^{b}	69.1±28.6^{c}	66.8±24.6^{ab}	1.39±0.51^{c}	1586.7±473.3^{c}	13.9±3.68^{a}	38.7±16.5^{a}	10.1±8.03^{a}	3.79±0.49^{b}	21.1±2.36^{b}	–18.97	12.95
	Sillago japonica	20	n.d.	2.54±1.42^{a}	24.8±9.57^{d}	2.43±2.19^{a}	55.2±9.13^{a}	0.67±0.22^{a}	549.6±222.7^{a}	11.1±6.33^{a}	62.8±37.8^{b}	22.2±21.1^{a}	2.17±1.00^{a}	25.4±6.45^{c}	–16.24	11.54
	Upeneus sulphureus	20	4.16±2.04^{b}	8.97±2.11^{c}	16.8±4.60^{c}	21.3±9.61^{b}	65.6±48.3^{ab}	1.74±0.42^{d}	1972.3±411.7^{d}	18.0±6.43^{a}	95.9±20.7^{c}	51.2±42.6^{b}	4.32±0.43^{cd}	14.8±1.18^{a}	–16.95	13.05

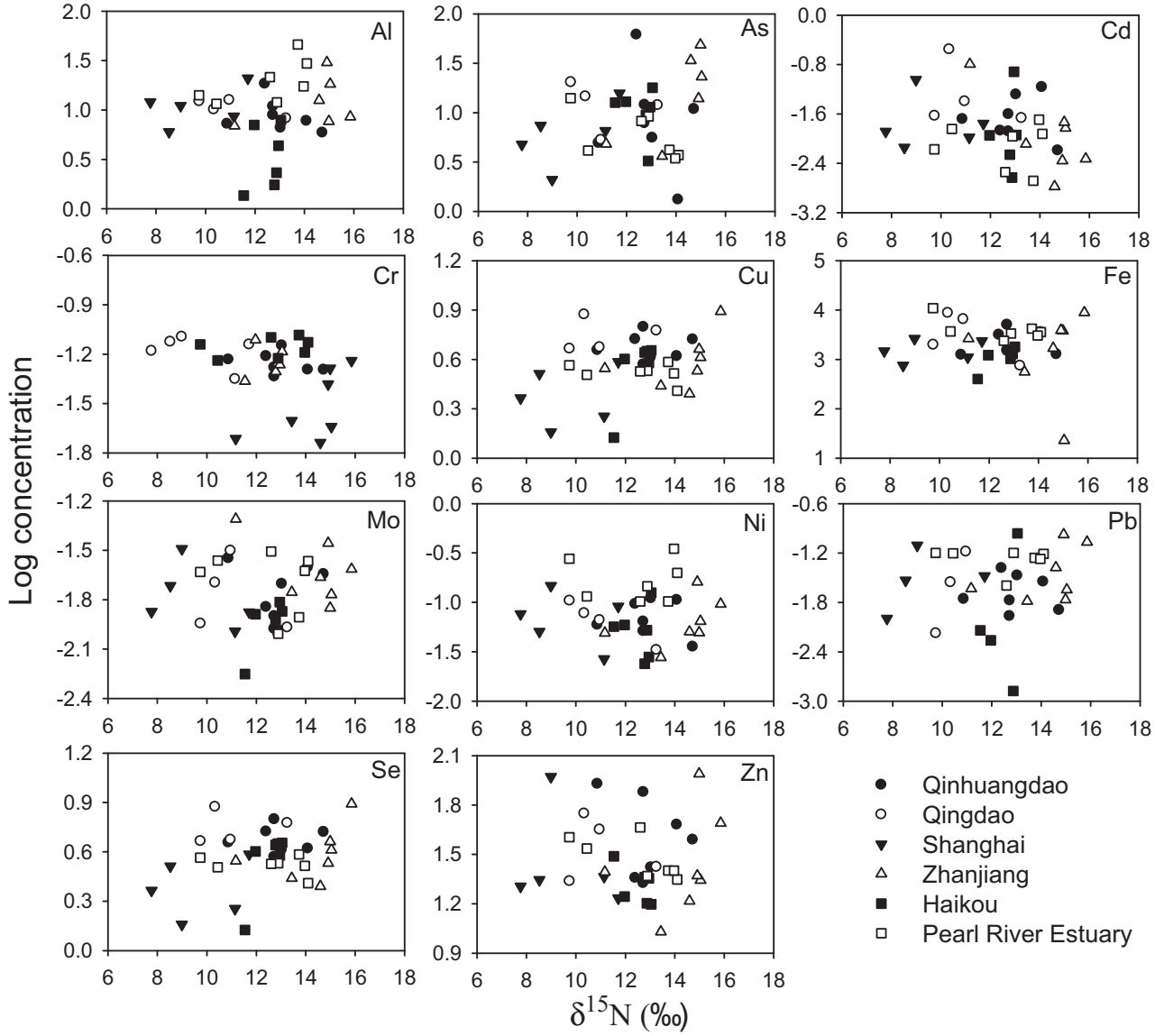

Fig. 2. Relationship between log-transformed trace elements concentrations and δ^{15}N values in marine wild fish from China Seas. Concentrations of Al, As, Cu, Fe, Se, and Zn were expressed as μg/g dry weight, and those of Ag, Cd, Cr, Mo, Ni, and Pb were expressed as ng/g dry weight.

compared with other areas, except Qingdao. The Pearl River Estuary had significant different δ^{15}N values compared with Qingdao, and Shanghai.

There was no significant relationship ($p > 0.05$) between the log concentrations of all trace elements in the fish muscles and the δ^{15}N values from each station, indicating no biomagnification of metals in the fish (Fig. 2).

3.4. Estimated exposure and hazards quotients of trace elements

The mean trace elements concentrations in fish muscles from different locations were used to calculate the daily intake of trace elements through marine fish consumption by Chinese people. FAO/WHO Expert Committee on Food Additives have set a PTWI of Cd as 7 μg/kg bw, a PTWI of Pb as 25 μg/kg bw, a PTWI of MeHg as 1.6 μg/kg bw for humans [14]. An average weight of 58.1 kg was assumed for a Chinese person based on the statistics on 158,666 Chinese from all provinces during a mean follow-up of 8.3 years [15]. On average, the daily consumption rate of marine fish is 3 g/person/day in China [13]. For As, its toxicity depends greatly on arsenic speciation, with the inorganic arsenic species being more toxic than the organic forms [16,17]. The U.S. EPA uses inorganic arsenic uptake by various seafood to determine the potential risk to human health [18], and thus only inorganic As was considered in the hazard calculations.

Table 2 shows that the HQ of Ag, As, Cd, Cr, Cu, Fe, Mo, Ni, Se, and Zn were all less than 1, and the EDI of fish species lead to trace elements consumption 3 to 11475 times lower than the RfD guidelines for trace elements studied, suggesting that people would not experience significant health risks from the intake of trace elements through the fish consumption. In our study, the fish were all approximately 10 cm and omnivorous, and there was no significant health risks.

4. Discussion

4.1. Geographic variance

Earlier studies largely reported trace elements concentrations in marine fish based on wet weight. Table 3 compares the trace

Table 2
Daily intake of trace elements through marine fish consumption by people in China. EDI: estimated daily intake; ADI: acceptable daily intake, calculated from the provisional tolerance weekly intake set by the Joint Food and Agriculture Organization/World Health Organization Expert Committee on Food Additives (2003); RfD: reference doses of trace elements as established by the United States Environmental Protection Agency (2011); Hazard quotient (HQ) = EDI/RfD. If the ratio is <1, there is no obvious risk.

Trace elements	Concentrations (μg/g ww)	EDI (μg/kg bw/day)	ADI (μg/kg bw/day)	Rfd (μg/kg bw/day)	Hazard quotient
Ag	0.095–1.49 (ng/g)	0.000–0.077	5	5	<0.01–0.02
As[a]	0.052–1.86	0.003–0.096	2.14	0.3	0.01–0.32
Cd	0.593–17.8 (ng/g)	0.000–0.001	1	1	<0.01
Cr	4.40–30.3 (ng/g)	0.000–0.001	–	3	<0.01
Cu	0.175–1.58	0.009–0.082	500	40	<0.01
Fe	118.4–2947.1	0.061–152.2	800	700	<0.01–0.22
Mo	2.19–20.4 (ng/g)	0.000–0.001	–	5	<0.01
Ni	5.58–115 (ng/g)	0.000–0.006	–	50	<0.01
Se	0.46–1.77	0.024–0.091	5	5	<0.01–0.02
Zn	3.70–19.8	0.191–1.021	300	300	<0.01

[a] Average concentration of inorganic As was estimated as 10% of total As (United States Food and Drug Administration, 1993).

elements concentrations in marine fish collected from different locations of the world. A wet/dry weight conversion factor of 4 can be used for easy comparison [7].

Among the 12 trace elements quantified in this study, Ag, Cu, Mo, Se, and Zn had no clear spatial differences among all the locations (from Northern to Southern parts). Several possibilities may explain such lack of spatial patterns for these 5 metals. First, there was probably no obvious source of metal input. Second, some of these trace elements are essential to the marine animals (Cu, Mo, Se, and Zn), and it is likely that these metals may be regulated by the fish during their bioaccumulation processes. For example, regulation of Cu and Zn by fish has been demonstrated by previous studies [19,20]. Whether marine fish can regulate Mo uptake is still unknown in the literature. In previous study, the Cu, Se, and Zn concentrations in fish were generally found to be within the range of 0.65–2.78 μg/g, 0.19–0.85 μg/g, and 38.8–93.4 μg/g, respectively. Our measurements of the marine wild fish in China were rather similar to these previous measurements (e.g., 0.51–7.0 μg/g Cu, 3.51–53.5 μg/g Zn from Aegean Sea and Mediterranean Sea [21]; 0.4–7.8 μg/g Cu, and 13.1–169 μg/g Zn from Zhejiang costal area [8]).

Among the remaining trace elements, Al, Cr, Ni, and Pb were found to be the highest in the Pearl River Estuary. Pearl River Delta (PRD) was the only estuary included in this study. Such high metal concentrations in fish collected from the PRD highlighted the intensive industrial activity in this region. Indeed, PRD exhibited the rapidest economic growth over the past two decades in China, and industrial pollution has reached a rather high level. It is interesting to note that these four metals (Al, Cr, Ni, and Pb) are all closely related to industrial activity such as electroplating, dyeing, paper manufacturing, tanning, bleaching, printing and other industries. Ip et al. [22] reported that the concentrations of metals in sixteen species of fish collected from the Pearl River Estuary were 110–4270 ng/g Cr ww, 170–2080 ng/g Ni ww, and 90–3070 ng/g Pb ww. Cheung et al. [9] also reported that the concentrations of ten marine fish species collected from the Pearl River Estuary were 40–220 ng/g Cr ww, 110–700 ng/g Ni ww, and 50–240 ng/g Pb ww. Meanwhile, increasing amounts of wastewater and other pollutants were discharged into the Pearl River Estuary without proper treatment [23]. In general, the Cr and Ni levels detected in the marine wild fish from China were lower than those measured elsewhere (e.g., 630–1740 ng/g Cr ww, 1140–3600 ng/g Ni ww from Black Sea [24]; 950–1980 ng/g Cr, 1920–5680 ng/g Ni, and 330–930 ng/g Pb from Black Sea and Aegean Sea [25]; <10–450 ng/g Cr, 180–2780 ng/g Ni, 30–1720 ng/g Pb from the Aegean and Mediterranean Seas [21]).Among the 8 locations, the lowest levels of Al, Fe, Pb were detected in the southern location (Haikou, Hainan Province). Such results were consistent with the fact that Haikou was the tourism city without too much industrial activity. The atmospheric deposition (automobile emissions and industrial discharges) in Haikou was taken into account in the assessment because atmospheric deposition is one of the principal pathways of transport for anthropogenic Pb. Since there were relatively few automobiles and industries, the Pb concentrations in marine fish from Haikou were the lowest among all the locations.

In our study, As was the most seriously concerned trace elements in the fish. The highest As levels were detected in Huilai and Zhanjiang, with the highest concentrations of 36.1 μg/g and 134 μg/g, respectively. It has been reported that As in fish muscles is mainly presented as arsenobetaine, which is non-toxic and the most stable form [26]. As is derived from some environmental elements such as rock decay, volcanic explosion, and mainly rooted in industry production, pesticides, coal combustion, mining, and smelting. Liu et al. [27] conducted an extensive environmental study of an abandoned tungsten mine in Shantou City, southern China. The As concentration reached up to 325 mg/L in the groundwater, and the maximum As concentrations in local food were 1.09, 2.38 and 0.60 μg/g for brown rice, vegetable and fish samples, respectively, suggesting that the local water resource and food have been severely contaminated with As. Interestingly, the highest levels of As were only found for the demersal fish species (*Cynoglossus joyneri* and *Trypauchen vagina*), which strongly suggested that sediment pollution and ingestion of benthic preys may contribute to such high levels of As in the fish. Wang et al. [28] reported that As content in the surface sediments of the Guangzhou section of the Pearl River in Southern China. The total As in the sediment samples averaged 24.6 μg/g and ranged from 16.7 to 33.4 μg/g. In previous studies, the As levels in marine fish were 0.01–70.9 μg/g in the Adriatic Sea [29], and 0.11–0.32 μg/g in the Black Sea [24], which were 2–400 times lower than those obtained in this study.

Cd in the marine wild fish from China Seas had very similar levels to those observed in the Mediterranean Sea (2–10 ng/g, ww) [30], Mauritanian coast, Atlantic Ocean (6.6 ng/g, ww) [31], Adriatic Sea (20–40 ng/g, ww) [32], and Aegean and Mediterranean Seas near Turkey (<10–390 ng/g, ww) [21]. In our study, Cd in the marine wild fish collected from the Northern parts of China were generally higher (4–9 fold) than that from the Southern China. Such higher concentrations may have been due to the higher industrial activity in the Northern parts of China. For example, Bohai Bay has been seriously contaminated with Cd and Zn. Luo et al. [33] reported that the surface sediments collected from the coastal and estuarine areas of the northern Bohai and Yellow Seas, China, were moderately polluted by Cd. As discussed above, the less clear spatial pattern of Zn was probably due to the regulation of this metal by the fish.

4.2. Differences of metal concentrations among different fish species and stable isotope analysis

In our study, a total of twenty-nine species were collected from different locations for metal analysis. Among the twenty-nine

Table 3
Comparison of trace element concentrations in fish from different area. dw: dry weight; ww: wet weight.

Location		As (μg/g)	Cd (ng/g)	Cr (ng/g)	Cu (μg/g)	Fe (μg/g)	Ni (ng/g)	Pb (ng/g)	Se (μg/g)	Zn (μg/g)	References
China Seas	dw	2.09–134	2.37–71.3	17.6–121	0.34–7.35	473–11788	22.3–461	2.69–290	1.84–7.41	10.4–79.1	This study
Zhejiang coastal area	dw	n.d.–30.4	4–384		0.4–7.8			32–568		13.08–168.8	Fang et al. (2004)
Black and Aegean Seas	dw		450–900	950–1980	0.73–1.83	68.6–163	1920–5680	330–930		35.4–106	Uluozlu et al. (2007)
Black Sea	ww	0.11–0.32	100–350	630–1740	0.65–2.78	36.2–145	1140–3600	280–870	0.19–0.63	38.8–93.4	Tuzen (2009)
Aegean and Mediterranean	ww		<10–390	<10–450	0.07–1.48	0.51–7.05	180–2780	30–1720		3.51–53.5	Türkmen et al. (2009)
Adriatic Sea	ww	0.01–70.9	1–850		0.001–57.3			1–340			Bilandžić et al. (2011)

species, a few species displayed rather contrasting patterns of metal accumulation as compared to the rest of the fish species. For example, *Cynoglossus joyneri* had very high Al, Cr, and Pb levels. The Cu levels in *Clupanodon thrissa* from Qinhuangdao, Qingdao, and Pearl River Estuary were all higher than the other species. Such differences of metal accumulation in marine fish may have been due to the different biokinetics of metals in these fish, as well as the different feeding ecology of the fish. Interestingly, these two species are both considered demersal, and the likely sources of metal accumulation may have been due to the trophic transfer of metals from their prey species such as invertebrates.

Another possible explanation for the inter-species difference in metal accumulation is the trophic level of fish. Previously, it has been well established that some metals such as Hg (methylmercury) and radiocesium were biomagnified during their trophic transfer, indicating that the difference of feeding habit may contribute to the difference of their tissue accumulation in fish. A few studies have also shown that the marine juveniles fish can possibly biomagnify Se and Zn during the trophic transfer process [34]. However, in our study, biomagnifications did not appear for the 12 trace elements. There was no significant correlation between the δ^{15}N and the trace elements concentration in marine fish species in this study. Similarly, Asante et al. [10] reported no correlation between δ^{15}N and trace elements in demersal marine organisms from shallow water and in pelagic species from deep water from the East China Sea. Ikemoto et al. [35] also found that trace elements such as V, Cr, Mn, Co, Cu, Zn, As, Sr, Mo, Ag, Cd, Sn, Sb, Cs, Ba, Tl, Pb, and Bi were not biomagnified or biodiluted through the food chain in the Mekong River Delta.

Previous studies have reported that trace elements concentrations in fish muscles varied widely among different fish species. Agusa et al. [36] reported that the highest levels of Co (1.55 μg/g), Cu (25.3 μg/g), Rb (3.53 μg/g), Ag (0.48 μg/g) and Sn (1.41 μg/g) were found in the black pomfrets (*Parastromateus niger*), and extremely high Zn concentration (953 μg/g) was found in the kawakawas (*Euthynnus affinis*). On the other hand, the javelin grunters (*Pomadasys kaakan*) showed the minimum concentrations of Mn (0.69 μg/g), Cu (2.62 μg/g), Zn (27.1 μg/g), Se (1.86 μg/g), Rb (0.67 μg/g), Mo (0.091 μg/g), Ag (0.012 μg/g), and Cs (<0.01 μg/g) from the coastal areas of Malaysia. Burger and Gochfeld [5] reported that flounder had the highest levels of As; tuna had the highest levels of Cd and Hg; and Chilean sea bass had the highest levels of Se in New Jersey. Falcó et al. [30] also reported different concentrations of Hg, Cd, Pb, As, Se, and Mn in fish purchased from markets in New Jersey and Catalonia, and concluded that there were significant interspecific differences for all metals. Again, such interspecies difference may have been due to the differences of geography, trophic level, size, foraging method/location, and the propensity of metals to undergo biomagnification in the food chain [5].

Our measurements of the stable isotope ratios in marine fish from the China Seas were generally similar to earlier studies. For instances, nitrogen and carbon stable isotope ratios of 128 specimens of 50 fish species in the Yellow Sea and the East China Sea ranged from 7.13‰ to 14.30‰ and from −23.14‰ to −15.71‰, respectively [37]. Asante et al. [10] reported that the arithmetic mean (AM) of δ^{15}N and δ^{13}C in fish from the East China Sea were 10.38–14.69‰ and −20.87 to −16.37‰, respectively. Spatial variations of δ^{13}C and δ^{15}N were obvious among some locations, and may be attributable to the different isotopic backgrounds of each area (i.e. isotopic differences in the first trophic level that are mirrored in the upper ones) and/or differences in the food habits and foraging habitats. A wide variability in the isotopic composition of Mediterranean littoral fish and marine protected area has also been reported [38,39]. We evaluated the biomagnifications of trace elements through δ^{15}N measurements. In the present study, no biomagnification was found among the 12 trace elements, similar with

previous studies. For example, Asante et al. [10] reported that there was no significant correlation between the concentrations of As and the δ^{15}N values in fish from the East China Sea. Ikemoto et al. [35] also found no biomagnification of As in fish from the Mekong River Delta. Previous studies have also shown that As decreased with trophic level because these elements were diluted by trophic transfer [40].

4.3. Risk to human

A comparison of measured concentrations of trace elements in marine fish (present study) and levels reported in other Chinese foodstuffs is possible. Cheung et al. [41] found that the Hg contents in most of the marine fish collected from local fish markets were 0.35–3.57 μg/g, ww. Some trace elements concentrations in marine fish were generally higher than the levels reported in other foodstuffs, e.g., As (0.10–0.24 μg/g, dw), Pb (1.38–3.88 μg/g, dw), and Zn (18.7–23.1 μg/g, dw) levels in mushroom [42]; Cu (0.214–0.875 μg/g, ww), Zn (0.742–2.56 μg/g, ww), Ni (0.026–0.075 μg/g, ww), Pb (0.009–0.018 μg/g, ww), and As (0.009–0.019 μg/g, ww) in vegetable oils [43]. Conversely, Cu and Cr levels in marine fish were lower than those (11.4–15.8 μg Cu/g, dw, 3.36–4.78 μg Cr/g, dw in mushroom [42].

FAO/WHO Expert Committee on Food Additives have set a PTWI of Cd as 7 μg/kg bw, a PTWI of Pb as 25 μg/kg bw, a PTWI of MeHg as 1.6 μg/kg bw for humans [14]. Our calculations suggested that the HQs of all trace elements examined in this study (except Al and Pb, which did not have the RfD values) were significantly less than 1, suggesting that the consumption of marine fish did not present any risk to humans. The calculated EDI of fish species led to trace elements consumption 3–11,475 times lower than the RfD guidelines, thus people would not experience significant health risks from the intake of trace elements through fish consumption. The average fish and seafood consumption of Chinese people (71 g/person/day according to the FAO) includes freshwater fish (29 g/person/day), shellfish (29 g/person/day), and marine fish (3 g/person/day). But care must be taken considering that most coastal people regularly consume large quantities of seafood. In Hong Kong, for example, the estimated daily consumption of marine fish is 25 g/day (or 8 times higher than the average Chinese consumption). Even with such high fish consumption, the EDI was lower than the established ADI (calculated from the PTWI). If only the total As concentrations were considered for the 4 marine fish species (*Cynoglossus joyneri*, *Trypauchen vagina*, *Gerreomorpha japonica*, *Zebrias zebra*), its HQ was greater than 1, indicating that there was a potential risk.

5. Conclusion

Accumulation of trace elements (such as Al, As, Cd, Cr, Ni, Pb) in food is a major safety health concern worldwide. The present study involved a large scale investigation of trace elements in marine wild fish in China Seas. The data indicated that trace elements levels had geographic differences, likely due to the differences of trace elements bioaccumulation and the sources of industrial and agriculture inputs. The distribution trend revealed the current economic status of development from the northern parts to the southern parts of China. The rapid economic development in the Pearl River Estuary led to a rather high concentration of Al, Cr, Ni, and Pb, whereas the most southern waters (Haikou) contained the lowest concentrations of Al, Fe, and Pb. Interestingly, Cd concentrations in the fish muscles from the northern sides were generally higher than those from the southern sides. For each marine fish species, demersal fish were more liable to enriching trace elements than the pelagic fish. Risk assessments indicated that human health risks associated with trace elements exposure via consumption of marine wild fish are negligible.

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References

[1] K. Pan, W.-X. Wang, Trace metal contamination in estuarine and coastal environments in China, Sci. Total Environ. (2011), doi:10.1016/j.scitotenv.2011.03.013.
[2] FAO technical guidelines for responsible fisheries. Health management for responsible movement of live aquatic animals, 2007.
[3] F. Kucuksezgin, O. Altay, E. Uluturhan, A. Kontas, Trace metal and organochlorine residue levels in red mullet (*Mullus barbatus*) from the eastern Aegean, Turkey, Water Res. 35 (2001) 2327–2332.
[4] M.A. Lewis, G.I. Scott, D.W. Bearden, R.L. Quarles, J. Moore, E.D. Strozier, S.K. Sivertsen, A.R. Dias, M. Sanders, Fish tissue quality in near-coastal areas of the Gulf of Mexico receiving point source discharges, Sci. Total Environ. 284 (2002) 249–261.
[5] J. Burger, M. Gochfeld, Heavy metals in commercial fish in New Jersey, Environ. Res. 99 (2005) 403–412.
[6] J. Kojadinovic, M. Potier, M. Le Corre, R.P. Cosson, P. Bustamante, Bioaccumulation of trace elements in pelagic fish from the Western Indian Ocean, Environ. Pollut. 146 (2007) 548–566.
[7] S. Onsanit, C. Ke, X. Wang, K.-J. Wang, W.-X. Wang, Trace elements in two marine fish cultured in fish cages in Fujian province, China, Environ. Pollut. 158 (2010) 1334–1342.
[8] J. Fang, K.X. Wang, J.L. Tang, M. Wang, S.J. Ren, H.Y. Wu, J. Wang, Copper, lead, zinc, cadmium, mercury, and arsenic in marine products of commerce from Zhejiang coastal area, China, May 1998, Bull. Environ. Contam. Toxicol. 73 (2004) 583–590.
[9] K.C. Cheung, H.M. Leung, M.H. Wong, Metal concentrations of common freshwater and marine fish from the Pearl River delta, South China, Arch. Environ. Contam. Toxicol. 54 (2008) 705–715.
[10] K.A. Asante, T. Agusa, H. Mochizuki, K. Ramu, S. Inoue, T. Kubodera, S. Takahashi, A. Subramanian, S. Tanabe, Trace elements and stable isotopes (δ^{13}C and δ^{15}N) in shallow and deep-water organisms from the East China Sea, Environ. Pollut. 156 (2008) 862–873.
[11] United States Environmental Protection Agency, Risk-based Concentration Table, April 2011, U.S. EPA, Region 3, Philadelphia, PA. http://www.epa.gov/reg3hwmd/risk/human/index.htm, 2011.
[12] Joint Food and Agriculture Organization/World Health Organization Expert Committee on Food Additives, Summary and Conclusions of the 61st Meeting of the Joint FAO/WHO Expert Committee on Food Additives, JECFA/61/Sc, Rome, Italy, 10–19.06.03. 1–22, 2003.
[13] Food Security Statistics: Food Consumption, Statistics Division, Food and Agricultural Organization of the United Nations, http://www.fao.org/es/ESS/faostat/foodsecurity/index_en.htm, 2008.
[14] FAO/WHO Expert Committee on Food Additives, WHO Technical Report Series 759, WHO, Geneva, Switzerland, 1989.
[15] D.F. Gu, J. He, X.F. Duan, K. Reynolds, X.G. Wu, J. Chen, G.Y. Huang, C.H. Chen, P.K. Whelton, Body weight and mortality among men and women in China, J. Am. Med. Assoc. 295 (2006) 776–783.
[16] W. Goessler, D. Kuehnelt, Analytical methods for the determination of arsenic and arsenic compounds in the environment, in: Environmental Chemistry of Arsenic, Marcedl Dekker, New York, USA, 2002, pp. 27–50.
[17] J.C. Ng, Environmental contamination of arsenic and its toxicological impact on humans, Environ. Chem. 2 (2005) 146–160.
[18] U.S. Environmental Protection Agency, Frame work for metals risk assessment, Washington, D.C.: U.S. EPA, 2007.
[19] L. Zhang, W.-X. Wang, Alteration of dissolved cadmium and zinc uptake kinetics by metal pre-exposure in the black sea bream (*Acanthopagrus schlegeli*), Environ. Toxicol. Chem. 25 (2006) 1312–1321.
[20] F. Dang, H. Zhong, W.-X. Wang, Copper uptake kinetics and regulation in a marine fish after waterborne copper acclimation, Aquat. Toxicol. 94 (2009) 238–244.
[21] M. Türkmen, A. Türkmen, Y. Tepe, Y. Töre, A. Ates, Determination of metals in fish species from Aegean and Mediterranean seas, Food Chem. 113 (2009) 233–237.
[22] C.C.M. Ip, X.-D. Li, G. Zhang, C.S.C. Wong, W.L. Zhang, Heavy metal and Pb isotopic compositions of aquatic organisms in the Pearl River Estuary, South China, Environ. Pollut. 138 (2005) 494–504.
[23] X.P. Huang, Application of the receptor model to research on heavy metal pollution of sediments in Lingdingyang Estuary, Tropic Oceanol. 14 (1995) 1–6 (in Chinese).

[24] M. Tuzen, Toxic and essential trace elemental contents in fish species from the Black Sea, Turkey, Food Chem. Toxicol. 47 (2009) 1785–1790.
[25] O.D. Uluozlu, M. Tuzen, D. Mendil, M. Soylak, Trace metal content in nine species of fish from the Black and Aegean Seas, Turkey, Food Chem. 104 (2007) 835–840.
[26] H. Amlund, K.A. Francesconi, C. Bethune, A.K. Lundebye, M.H.G. Berntssen, Accumulation and elimination of dietary arsenobetaine in two species of fish, Atlantic salmon (*Salmo sakar* L.) and Atlantic cod (*Gadus morhua* L.), Environ. Toxicol. Chem. 25 (2006) 1787–1794.
[27] C.P. Liu, C.L. Luo, Y. Gao, F.B. Li, L.W. Lin, C.A. Wu, X.D. Li, Arsenic contamination and potential health risk implications at an abandoned tungsten mine, southern China, Environ. Pollut. 158 (2010) 820–826.
[28] S.L. Wang, X.Z. Cao, C.Y. Lin, X.G. Chen, Arsenic content and fractionation in the surface sediments of the Guangzhou section of the Pearl River in Southern China, J. Hazard. Mater. 183 (2010) 264–270.
[29] N. Bilandžić, M. Đokić, M. Sedak, Metal content determination in four fish species from the Adriatic Sea, Food Chem. 124 (2011) 1005–1010.
[30] G. Falcó, J.M. Llobet, A. Bocio, J.L. Domingo, Daily intake of arsenic, cadmium, mercury, and lead by consumption of edible marine species, J. Agric. Food Chem. 54 (2006) 6106–6112.
[31] M. Roméo, Y. Siau, Z. Sidoumou, M. Gnassia-Barelli, Heavy metal distribution in different fish species from the Mauritania Coast, Sci. Total Environ. 232 (1999) 169–175.
[32] M.M. Storelli, Potential human health risks from metals (Hg, Cd, and Pb) and polychlorinated biphenyls (PCBs) via seafood consumption: estimation of target hazard quotients (THQs) and toxic equivalents (TEQs), Food Chem. Toxicol. 46 (2008) 2782–2788.
[33] W. Luo, Y.L. Lu, T.Y. Wang, W.Y. Hu, W.T. Jiao, J.E. Naile, J.S. Khim, J.P. Giesy, Ecological risk assessment of arsenic and metals in sediments of coastal areas of northern Bohai and Yellow Seas, China, Ambio 39 (2010) 367–375.
[34] L. Zhang, W.-X. Wang, Size-dependence of the potential for metal biomagnification in early life stages of marine fishes, Environ. Toxicol. Chem. 26 (2007) 787–794.
[35] T. Ikemoto, N.P.C. Tu, N. Okuda, A. Iwata, K. Omori, S. Tanabe, B.C. Tuyen, I. Takeuchi, Biomagnification of trace elements in the aquatic food web in the Mekong Delta, south Vietnam using stable carbon and nitrogen isotope analysis, Arch. Environ. Contam. Toxicol. 54 (2008) 504–515.
[36] T. Agusa, T. Kunito, G. Yasunaga, H. Iwata, A. Subramanian, A. Ismail, S. Tanabe, Concentrations of trace elements in marine fish and its risk assessment in Malaysia, Mar. Pollut. Bull. 51 (2005) 896–911.
[37] C. Deling, L. Hongyan, T. Gisheng, S. Yao, Establishment of trophic continuum in the food web of the Yellow Sea and East China Sea ecosystem: insight from carbon and nitrogen stable isotopes, Sci. China Ser. C: Life Sci. 48 (2005) 531–539.
[38] S. Deudero, J. Pinnegar, N. Polunin, G. Morey, B. Morales-Nin, Spatial variation and ontogenic shifts in the isotopic composition of Mediterranean littoral fishes, Mar. Biol. 145 (2004) 971–981.
[39] S. Vizzini, A. Mazzola, Stable isotopes and trophic positions of littoral fishes from a Mediterranean marine protected area, Environ. Biol. Fish. 84 (2009) 13–25.
[40] W. Maher, E. Butler, Arsenic in the marine environment, Appl. Organomet. Chem. 2 (1998) 191–214.
[41] K.C. Cheung, H.M. Leung, M.H. Wong, Metal concentrations of common freshwater and marine fish from the Pearl River Delta, South China, Arch. Environ. Contam. Toxicol. (2008) 705–715.
[42] T. Li, Y.Z. Wang, J. Zhang, Y.L. Zhao, H.G. Liu, Trace element content of Boletus tomentipes mushroom collected from Yunnan, China, Food Chem. 127 (2011) 1828–1830.
[43] F.K. Zhu, W.X. Fan, X.J. Wang, L. Qu, S.W. Yao, Health risk assessment of eight heavy metals in nine varieties of edible vegetable oils consumed in China, Food Chem. Toxicol. 49 (2011) 3081–3085.