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Determination of trace metals and analysis of arsenic species in tropical marine fishes from Spratly islands

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A B S T R A C T

Trace metal contents in 38 species of tropical marine fishes harvested from the Spratly islands of China were determined by microwave digestion and inductively coupled plasma mass spectrometry analysis. Arsenic species were determined by high-performance liquid chromatography and inductively coupled plasma mass spectrometry analysis. The average levels of Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Pb, and U in the fish samples were 1.683, 0.350, 0.367, 2.954, 36.615, 0.087, 0.319, 1.566, 21.946, 20.845, 2.526, 3.583, 0.225, 0.140, and 0.061 $mg \cdot kg^{-1}$, respectively; Fe, Zn, and As were found at high concentrations. The trace metals exhibited significant positive correlation between each other, with r value of 0.610–0.852. Further analysis indicated that AsB (8.560–31.020 $mg \cdot kg^{-1}$) was the dominant arsenic species in the fish samples and accounted for 31.48% to 47.24% of the total arsenic. As(III) and As(V) were detected at low concentrations, indicating minimal arsenic toxicity.

Heavy metal pollution in marine environments is a serious environmental problem (Jambeck et al., 2015; Das et al., 2007; Naser, 2013). The accumulation of heavy metals in marine organisms may affect human health through the food chain (Zmozinski et al., 2013; Modibbo et al., 2014). Therefore, scholars have focused on heavy metal accumulation in seafood and fishes (Darko et al., 2016; Yang et al., 2014; Stankovic and Jovic, 2012). Fishes are often at the top of the aquatic food chain and accumulate large amounts of heavy metals from the marine environments (Mansour and Sidky, 2002; Low et al., 2015). The concentration and degree of heavy metal accumulation in fishes are affected by nutritional status, biological variables (e.g., species), and heavy metal concentrations in seawater and sediments. Moreover, the bioaccumulation of heavy metals can be used as an index of the pollution status of relevant seawater body to study the biological role of metals present at high levels in aquatic organisms, especially fish (Awheda et al., 2015; Authman et al., 2015; Omar et al., 2014).

The Spratly islands, which are included in the major archipelagos in the South China Sea (Li et al., 2017), contain abundant fish resources. Approximately 2927 marine species exist in the Spratly island sea and include 524 marine fish species (Rosenberg and Stahlschmidt, 2011; Qiu et al., 2010). In recent years, tourism and the increasing industrialization of neighboring countries have led to severe disruption of native flora and fauna, over-exploitation of natural resources, and environmental pollution (Mora et al., 2011; Dorman et al., 2016). Many activities adversely affect local marine organisms (Li et al., 2016). In this regard, the conservation of Spratly island ecosystems has gained increasing attention. However, limited information is available regarding trace metal content in fish harvested from the Spratly island seas.

Metals, such as As, Cd, Hg, and Pb, are not essential and toxic even at trace levels, whereas V, Fe, Zn, Se, Co, Cu, and Mn are metals vital to biological systems (Abadi et al., 2015; Kalay and Canli, 2000). The levels of heavy metals in fish samples have been widely investigated because of their effects on human health. Moreover, the presence of several arsenic species in seafood has been increasingly studied because the toxicity of As depends its chemical species (Zhang et al., 2012); among As species, arsenobetaine (AsB) and arsenocholine (AsC) are considered nontoxic. Arsenic species, such as monomethylarsonic acid (MMA) and dimethylarsenic acid (DMA), are slightly toxic to humans, whereas inorganic species, such as arsenite [As(III)] and arsenate [As(V)], are the most toxic (Geng et al., 2009; Feldmann and Krupp, 2011; Leufroy et al., 2011; Zhang et al., 2016).

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Heavy metal enrichment in aquaculture may pose a potential health risk. As such, we investigated and evaluated the levels of trace metals and arsenic species in fish samples collected from the Spratly island sea. This study mainly aims to: (1) test the total concentration of 15 trace metals in 38 species of tropical fishes, (2) evaluate the correlation and distribution characteristic of all trace metals, (3) explore differences in distribution pattern and levels of different arsenic species, and (4) assess the contamination degree of fish in the Spratly island sea area. This study is the first to analyze the content and distribution of trace metals and arsenic species in different tropical marine fishes in the Spratly island sea. Our study can provide initial data for further investigations on trace metals and health assessment of tropical marine lives in the Spratly islands.

Therefore, thirty eight different species of fish were collected from the Spratly islands of China during a specific survey voyage in 2016. All alive fish species were frozen immediately and taken to laboratory under − 20 °C after being identified. In the laboratory, all samples were firstly freeze-dried, ground, and sifted through an 80 mesh porous sieve before analysis. Then, approximately 0.5 g of sample was digested with 6 mL of 65% HNO_3 (Merck) and 2 mL of concentrated H_2O_2 (Merck) in a microwave digestion system (CEM, digestion procedures in Table 1) and diluted to 25 mL by adding double deionized water. Blank digestion was also conducted through the same method. During test, the concentrations of Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Pb, and U were analyzed using an Agilent 7500a ICP-MS system with 50 μg·L^{-1} Li, Sc, Ge, Y, In, Tb, and Bi (Agilent Technologies, USA) added online as internal standards to correct for matrix effects and instrumental drift.

During test, the accuracy of microwave digestion/ICP-MS method was verified by analysis of certified reference materials (GBW10050 GSB-28, IGGE, China). The reference substance of shrimp tissue (GBW10050 GSB-28, IGGE, China) was treated and analyzed in the same way as all samples. The analysis results (Al: 273.6 mg·kg^{-1}, V: 0.22 mg·kg^{-1}, Cr: 0.36 mg·kg^{-1}, Mn: 8.12 mg·kg^{-1}, Fe: 103 mg·kg^{-1}, Co: 0.05 mg·kg^{-1}, Ni: 0.242 mg·kg^{-1}, Cu: 10.08 mg·kg^{-1}, Zn: 71 mg·kg^{-1}, As: 2.76 mg·kg^{-1}, Se: 5.32 mg·kg^{-1}, Mo: 0.04 mg·kg^{-1}, Cd: 0.036 mg·kg^{-1}, Pb: 0.187 mg·kg^{-1}, and U:0.0089 mg·kg^{-1}) are consistent with the certified values (Al: 290.0 mg·kg^{-1}, V: 0.24 mg·kg^{-1}, Cr: 0.35 mg·kg^{-1}, Mn: 8.9 mg·kg^{-1}, Fe: 112 mg·kg^{-1}, Co: 0.044 mg·kg^{-1}, Ni: 0.23 mg·kg^{-1}, Cu: 10.3 mg·kg^{-1}, Zn: 76 mg·kg^{-1}, As: 2.5 mg·kg^{-1}, Se: 5.1 mg·kg^{-1}, Mo: 0.037 mg·kg^{-1}, Cd: 0.039 mg·kg^{-1}, Pb: 0.20 mg·kg^{-1}, and U: 0.0097 mg·kg^{-1} of dry weight). The results for standard reference substance showed that element recovery ranged from 91.24% to 113.64% (n = 3). The standard deviation was less than 6%, proving the good repeatability of the methods.

Information about trace element concentrations in fish species is important for both environmental management and human consumption. The concentrations of trace metals in fish species collected from the Spratly islands are illustrated in Table 2. The contents of trace metals in all fish samples were as follows: 0.045–6.393 mg·kg^{-1} for Al, 0.040–3.312 mg·kg^{-1} for V, 0.122–0.947 mg·kg^{-1} for Cr, 0.350–14.300 mg·kg^{-1} for Mn, 13.400–146.700 mg·kg^{-1} for Fe, 0.007–0.458 mg·kg^{-1} for cobalt (Co), 0.029–3.234 mg·kg^{-1} for nickel (Ni), 0.487–5.144 mg·kg^{-1} for Cu, 8.662–54.520 mg·kg^{-1} for Zn, 1.511–65.660 mg·kg^{-1} for As, 0.964–4.959 mg·kg^{-1} for Se, 0.027–39.420 mg·kg^{-1} for Mo, 0.002–1.301 mg·kg^{-1} for Cd, 0.012–0.769 mg·kg^{-1} for Pb, and ND–0.415 mg·kg^{-1} for U. The average range of trace metals followed the order of Fe > Zn > As > Mo > Mn > Se > Al > Cu > Cr > V > Ni > Cd > Pb > Co > U. The highest metal concentrations were found in *Paraluteres prionurus Bleeker* (Al, Cu, Zn, and Pb), *Gobiidae* (V), *Pervagor melanocephalus* (Cr), *Brittle star* (Mn, Co, Ni, Cd, and U), *Gymnothorax reticularis Bloch* (Fe), *Cheilinus rhodochrous* (As), and *Gnathodentex aureolineatus* (Se and Mo). The lowest concentrations of trace metals were as follows: 0.045 mg·kg^{-1} Al, 13.400 mg·kg^{-1} Fe, 0.002 mg·kg^{-1} Cd, 0.012 mg·kg^{-1} Pb, and 0.029 mg·kg^{-1} Ni in *Aluterus scriptus*; 0.040 mg·kg^{-1} V in *Cypselurus katoptron*; 0.122 mg·kg^{-1} Cr and 0.007 mg·kg^{-1} Co in *T. quinquevittatum*; 0.350 mg·kg^{-1} Mn and 1.511 mg·kg^{-1} As in *Kyphosus lembus*; 0.487 mg·kg^{-1} Cu in *O. meleagris*; 8.662 mg·kg^{-1} Zn in *Sufflamen fraenatus*; 0.964 mg·kg^{-1} Se in *C. striatus*; and 0.027 mg·kg^{-1} Mo in *Lutjanus kasmira*.

The concentrations of V, Mn, Fe, Cu, Zn, and Cd are lower than the United States Environmental Protection Agency (USEPA) risk-based concentrations (V: 6.8 mg·kg^{-1}, Mn: 190 mg·kg^{-1}, Fe: 950 mg·kg^{-1}, Cu: 54 mg·kg^{-1}, Zn: 410 mg·kg^{-1}, and Cd: 1.4 mg·kg^{-1}). In some fishes, the concentrations of Co, As, and Se are slightly higher than the USEPA risk-based values (Co: 0.41 mg·kg^{-1}, As: 0.41 mg·kg^{-1}, and Se: 6.8 mg·kg^{-1})(USEPA, 2010). The samples were compared with those collected from the Fisheries Research Institute at Chu-Pei (Taiwan), which is the designated reference site free from anthropogenic emissions; the reference samples possess the following: Mn: 0.3 mg·kg^{-1}, Cu: 0.3 mg·kg^{-1}, Zn: 12 mg·kg^{-1}, As: 0.1 mg·kg^{-1}, Se: 0.17 mg·kg^{-1}, and Pb: 0.04 mg·kg^{-1} (Ling et al., 2009). The amounts of Mn, Cu, Zn, As, Se, and Pb in fish are higher than the base values. In particular, high As levels could be due to natural variations related to geographical origin.

All trace metal distribution characteristics in fishes are shown in Fig. 1. The mean concentrations of Al, Mn, Fe, Zn, As, Se, and Mo were high. The normalized calculation results of all metal contents (Fig. 2) showed that Fe (39.26%), Zn (23.53%), and As (22.35%) exhibited the highest distribution ratios, and the total ratio of other elements was 14.86%.

The correlation coefficient among the selected heavy metals is presented in Table 3. Significant positive correlations were obtained between Mn and V (r = 0.610), Fe and Al (r = 0.749), Co and Mn (r = 0.718), Ni and Mn/Co (r = 0.648 and 0.830), Cu and Al (r = 0.650), Zn and Mn/Fe (r = 0.625 and 0.612), Cd and Mn/Co/Ni (r = 0.780, 0.648 and 0.698), Pb and Al/Fe/Cd (r = 0.734, 0.697 and 0.664), and U and Ni (r = 0.852). This finding indicates the same or similar source input. Mo, As, and Se showed a negative correlation with the other metals.

In the present study, a sequential procedure was used to extract different arsenic species to analyze the distribution pattern and levels of different arsenic species. The extraction process involved three steps, which produced three As fractions, namely, nonpolar ($As_{nonpolar}$) extracted by acetone, polar (As_{polar}) extracted by methanol/H_2O, and inorganic arsenic species ($As_{inorganic}$) extracted by 0.05 mol/L HCl. Arsenic species mainly included AsIII, AsV, MMA, DMA, AsB, and AsC. Speciation analysis of arsenic species was performed by HPLC-ICP-MS with deionized water and 50 mM $(NH_4)_2CO_3$ as mobile phase. Six arsenic species were effectively and ideally separated under gradient elution (0–15 min linear gradient from 100%A to 100%B) by using mobile phase at low initial concentration and high elution rate (1.5 mL/

Table 1
The working parameters of microwave digestion.

Stage	Power/W		Temperature	Ramp	Hold
	Max	%	T/°C	t/min	t/min
1	1500	100	100	3:00	3:00
2	1500	100	150	7:00	3:00
3	1500	100	170	5:00	3:00
4	1500	100	190	5:00	10:00

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