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Arsenic speciation in wild marine organisms and a health risk assessment in a subtropical bay of China

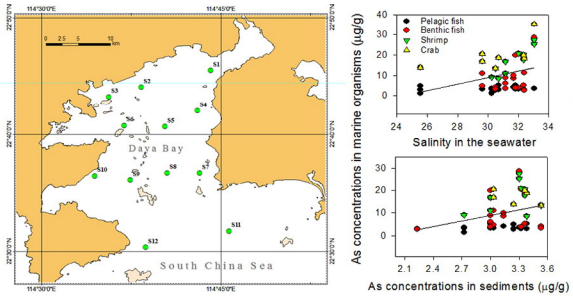
Wei Zhang [a], Zhiqiang Guo [c], Dongdong Song [a,b], Sen Du [a,b], Li Zhang [a,*]

[a] Key Laboratory of Tropical Marine Bio-resources and Ecology, Guangdong Provincial Key Laboratory of Applied Marine Biology, South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou 510301, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China
[c] State Key Laboratory of Marine Resource Utilization in South China Sea, College of Oceanology, Hainan University, Haikou 570228, China

HIGHLIGHTS

- The arsenic features within seawater, sediments, and organisms and surrounding salinity were investigated.
- Arsenobetaine was the most dominant form of arsenic found in all wild marine organisms.
- The high arsenic bioaccumulation in the wild marine organisms was due to the high arsenic in sediments and the high salinity.
- The inorganic arsenic, estimating the hazards, measured in all wild marine organisms indicated no health risks.

GRAPHICAL ABSTRACT



Trace elements	Average concentration (μg/g dw)	Hazard quotient
Total As		
Pelagic fish	1.22-5.23	0.05-0.23
Benthic fish	3.45-28.6	0.15-1.23
Shrimp	8.52-27.6	3.54-11.5
Crab	13.4-35.1	5.57-14.6
Inorganic As		
Marine fish	0.03-0.23	0.000-0.010
Shrimp/Crab	0.03-0.13	0.013-0.053
AsB		
Marine fish	1.19-28.4	No hazard
Shrimp/Crab	8.49-35.0	No hazard

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ABSTRACT

The total arsenic (As) and As species were analyzed in 19 species of wild marine organisms collected from 12 locations in Daya Bay, China; additionally, both the levels of As in the seawater and sediments and the salinity were investigated. The greatest level of As was found in crabs (13.4–35.1 μg/g), followed by shrimps (8.52–27.6 μg/g), benthic fish (3.45–28.6 μg/g), and pelagic fish (1.22–5.23 μg/g). There were significantly positive correlations between the As concentrations in the benthic fish *Callionymus richardsonii*/shrimp *Metapenaeopsis palmensis* and those in sediments, indicating that As levels in them were highly dependent on those in the sediments. Arsenobetaine (AsB) (87.3–99.8%) was the most dominant form of As found in all marine organisms. In benthic fish and shrimp, the bioaccumulation of As, especially AsB, was positively correlated with the salinity of the seawater, indicating that the salinity could control the transfer of As. The calculated hazard quotients (HQs) of the inorganic As in the marine organisms were all <1; thus, there was no apparent health hazard through the consumption of wild marine organisms.

1. Introduction

Arsenic (As) is a well-known metalloid that poses risks to human health in many places throughout the world (Duncan et al., 2015; Wang et al., 2014). The World Health Organization estimated in 2001 that about 130 million people worldwide are exposed to groundwater with As concentration above 50 μg/L, including Bangladesh, India, China, and USA (van Halem et al., 2009). Arsenic possesses a very complex chemistry in marine environments. The form of As that exists in the environment decides its fate, toxicity, and bioavailability (Bissen and Frimmel, 2003). Determining the form of As that is present is critical when assessing the risks it might pose (Francesconi, 2010; Lorenzana et al., 2009; Molin et al., 2012; Saunders et al., 2011). Therefore, arsenic

* Corresponding author.
E-mail address: zhangli@scsio.ac.cn (L. Zhang).

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speciation studies are necessary to identify the toxic and non-toxic portions of As and for health risk assessment.

As a result of human activities, there is a trend toward enhanced concentrations of certain pollutants in the bay, such as metalloid As (Islam and Tanaka, 2004). In a recent study on trace element contamination in wild marine fish collected from Chinese coastal waters, arsenic was the most serious identified trace element in the marine fish. The highest levels of As were found in the demersal fish species (*Cynoglossus joyneri* and *Trypauchen vagina*), which strongly demonstrated that sediment pollution and ingestion of benthic prey may contribute to such high As levels in marine fish (Zhang and Wang, 2012). According to earlier studies, there are different reasons for the high As bioaccumulation in organisms, including human activities (Hong et al., 2014; Liu et al., 2010) and the transfer of As from sediment or food (Kirby and Maher, 2002; Miao et al., 2012; Zhang and Wang, 2012). Furthermore, salinity may influence the concentration and fate of As in estuaries and continental shelves (Rahman et al., 2012). In the present study, in addition to human activities and sediment/food pollution, we hypothesized that natural processes, mainly salinity, also influenced the bioaccumulation and transfer of As in marine organisms.

Coastal bays, which are areas of active land-ocean interaction, are sensitive to anthropogenic activities and natural processes (Li et al., 2007). Daya Bay is a semi-enclosed shallow bay located in a highly industrial area and is deemed one of the most polluted coastal areas in China (Yu et al., 2010). Until now, in situ data on the multiple reasons for As bioaccumulation in marine organisms are scarce. Therefore, more field monitoring data are required to improve our current understanding of the multiple reasons for As bioaccumulation in wild marine organisms and to assess the human health risk posed by As.

In the present study, we surveyed the behavior of As in Daya Bay to i) investigate the As concentrations in the seawater, sediment, and organisms that were collected from 12 stations in the bay; ii) quantify the distribution of As species in wild marine organisms; and iii) determine the effects of seawater, sediment, and salinity in Daya Bay on the transfer of As. Meanwhile, stable isotopes of carbon ($\delta^{13}C$) were applied as a tool to track the food sources of marine organisms. Human health risk assessments for the Chinese people that consume wild marine organisms were also carried out. Therefore, characterizing the As features within seawater, sediments, and organisms and assessing the surrounding salinity could provide insights into the multiple causes of high As bioaccumulation in wild marine organisms and whether a human health risk is present.

2. Materials and methods

2.1. Sampling study sites

This work was undertaken in a typical subtropical bay, Daya Bay, on the south coast of China. This bay was chosen to represent important economic development districts, population density, and fishery production of many marine biota species in Guangdong Province (Chen et al., 2010). Fig. 1 shows the sampling sites in Daya Bay. Marine organisms (fishes, shrimps and crabs) were collected from 12 locations in the Daya Bay in May 2016. Sites were selected based on how well they represented local fishing patterns. The target species are frequently captured for human consumption.

2.2. Sampling

Surface and bottom seawater samples were collected using a hydrophore, and after filtration through a 0.45 μm filtration membrane, samples were loaded into a 250 mL polyethylene bottle. The surface sediments were collected with a bottom sampler. At each station, fishes, shrimps, and crabs were collected using a dredge to trawl for 30 min at a speed of 3 knots. Then, they were immediately placed into sealed polyethylene bags and stored in a −20 °C refrigerator for transport back to the laboratory. Fish, shrimp, and crab samples were thawed at room temperature and carefully dissected to obtain muscle tissues. Muscle is the most important tissue for human consumption. Muscles were freeze-dried and homogenized for the determination of the total As and As species.

2.3. Chemicals, reagents, total As and As species analysis

The methods for analyzing the total As and As speciation followed those of Zhang et al., 2015. The veracity of the digestion method and the extraction efficiency was assessed by analyzing the tuna fish standard reference material (SRM) (BCR-627, Institute for Reference Materials and Measurements, Geel, Belgium). The recovery was 94–101% for total As, 92–102% for arsenobetaine (AsB), and 72–84% for dimethylarsinic acid (DMA). Spikes were used to validate the recovery of other As forms, and the recovery of monomethylarsonic acid (MMA), As(V), and As(III) was 85–91%, 79–93%, and 82–95%, respectively.

2.4. Stable isotope analysis

The methods for stable isotope analysis followed those of Zhang and Wang (2012). The values for $\delta^{13}C$ were calculated using the standard delta (δ) notation in parts per thousand (‰), as follows:

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

where X represents $\delta^{13}C$, and R represents the relevant ratio $\delta^{13}C/^{12}C$. The $R_{standard}$ values came from Pee Dee Belemnite for $\delta^{13}C$.

2.5. Human exposure assessment

The methods for human exposure assessment were described in Zhang and Wang (2012). The estimated daily intake (EDI) (μg/kg/day) was calculated utilizing the following formula:

$$EDI = C_{seafood} \times [dc_{seafood}/bw]$$

where $C_{seafood}$ = average As concentration in the muscle of marine organisms (μg/g wet weight), $dc_{seafood}$ = daily consumption of marine organisms (g/day) as recorded by the FAO (2008), and bw = mean body weight (kg) of the target population. In the present study, the hazard quotient (HQ) was used for health risk assessment through consumption of marine organisms. The HQ was calculated as the EDI divided by the reference dose (RfD). There was no obvious risk if the HQ was <1. A wet/dry weight conversion factor of 4 was used Onsanit et al., 2010.

2.6. Statistical analysis

SPSS version 16.0 was utilized for the statistical analysis. The results were expressed as the means ± standard deviation (means ± SD). The differences were tested using a one-way analysis of variance (ANOVA) followed by a least significant difference (LSD) test. A probability level (p-value) of <0.05 was regarded as statistically significant. The regression coefficients between the As concentrations in the seawater/sediments, the salinity of the seawater and the marine organisms were analyzed via SigmaPlot 10.0.

3. Results and discussion

3.1. Arsenic concentrations in seawater, sediment, and marine organisms

The As concentrations (dissolved phase) in the surface seawater ranged from 2.81 to 4.48 μg/L, and those in the bottom seawater ranged from 1.78 to 3.42 μg/L (Table 1). In the surface sediment, the As