

# Heavy metals in sediments and fishery catches from the Beibu Gulf, China: bioaccumulation, potential risks, and human

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**Abstract.** In this study, 3 species of fishery catches (*Pennahia macrocephalus*, *Saurida tumbil*, and *Upeneus sulphureus*) and sediments were collected from the Beibu Gulf to identify the residual levels, human health risk, and ecological risk of HMs (As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, and Zn). The average concentrations (dry weight) of As, Cd, Cr, Cu, Mn, Ni, Pb, and Zn in the three species of fish were recorded as follows: 10.94, 0.11, 0.55, 2.00, 5.80, 0.47, 0.39, and 41.70 mg/kg, respectively. The health risk assessment results indicated that adults who consume these organisms could encounter carcinogenic health hazards, while children consuming these species may experience notable negative health effects. The contents of studied HMs reached China's national first-class benchmark of marine sediment quality. The ecological risk index (RI) of HMs from surface sediments ranged from 17.77 to 133.88, with a mean value of 56.45, which portrayed minor potential.

## 1 Introduction

With economic growth, population increase, and urbanization, an increasing amount of pollutants are being introduced into water bodies, primarily through various sources [1]. The significant toxicity, extended residual period, easy bio-absorption, and difficult degradation of heavy metals (HMs) have garnered significant interest [2]. Furthermore, HMs pose a threat to water ecosystems, bioaccumulate in marine life, and can be transferred to humans via food web [2]. Analyzing HM levels in organism aids in uncovering the contamination extent of marine life within the HM-infested environment.

In recent years, many studies have revealed contamination in the waters of the Beibu Gulf [3]. However, limited information exists regarding HM pollution in the area's sediments and main species. Moreover, with the ongoing reform of the Beibu Gulf Economic Zone, there is a potential for heightened environmental pollution in its marine ecosystem. This situation hinders a comprehensive assessment of the impact of economic development on the environment and impedes rational planning for future economic growth.

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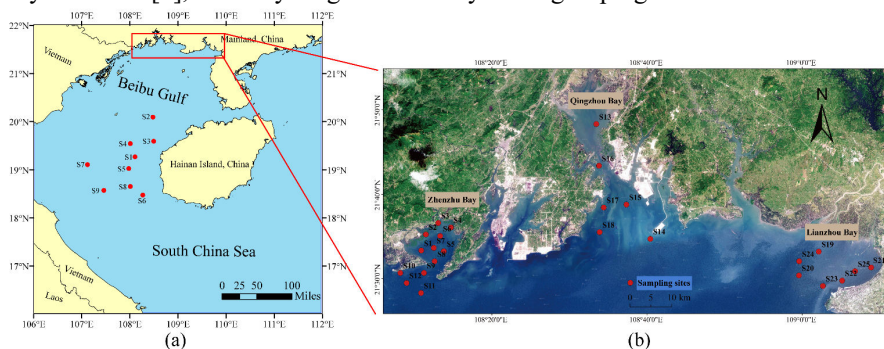
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This study aims to: (1) assess the HM contents in marine fish and associated health risks from consuming organisms, and (2) investigate HM concentrations and ecological risks in surface sediments. These efforts are intended to raise public awareness of health risks and provide a scientific basis for the management and protection of the Beibu Gulf.

## 2 Methodology

### 2.1 Sample preparation

In 2022, fishery catches were gathered for analysis through trawls and stow nets (Figure 1a), including 32 individuals of *S. tumbil* (*S.t.*), 34 of *P. macrocephalus* (*P.m.*), and 28 of *U. sulphureus* (*U.s.*). Sediment samples were obtained through Peterson sediment sampler from the major bays in the Beibu Gulf, China (Figure 1b). Following the Specification for Marine Surveys in China [4], the body lengths of fishery catch groupings are shown in Table 1.



**Fig. 1.** Distribution of sampling sites of fish (a) and sediments (b) from the Beibu Gulf.

**Table 1.** Length grouping information of three fishes from the Beibu Gulf.

Species	Group (mm)	Species	Group (mm)	Species	Group (mm)
<i>S.t.</i>	G 1: <120	<i>P.m.</i>	G 1: <70	<i>U.m.</i>	G 1: <100
	G 2: 121-150		G 2: 71-100		G 2: 101-115
	G 3: 151-180		G 3: 101-130		G 3: 116-130
	G 4: 181-210		G 4: 131-160		G 4: >130
	G 5: >211		G 5: >160		

Upon return to the laboratory, fish and sediment samples underwent freeze-drying (Scientz-10N, Scientz, China) at  $-80\text{ }^{\circ}\text{C}$  and were subsequently ground using an agate mortar. Sample pre-treatment involved microwave digestion following the procedure outlined by Yang et al. [3]. The levels of HMs were quantified using ICP-MS (Elan DRC II, Perkin Elmer, USA), while Hg levels were detected via AFS (Titan AFS-610A, China). The statistical software SPSS 20.0 (IBM Corp., USA), Origin 2021 (OriginLab Corp., USA), and Microsoft Excel 2019 (Microsoft Corp., USA) were utilized to conduct statistical analysis for the present study.

### 2.2 Human health risk and ecological potential risks

Total Hazard Quotient (THQ) and Total Cancer Risk (TCR), which are the arithmetic sum of HQ and CR, respectively, were utilized to evaluate non-carcinogenic and carcinogenic health risks posed by HM in fish for human intake [5]. Formulas were as follows [3,6]:

$$HQ = (ED \times EF \times FIR \times MC) / BW \times AT \times RFD \quad (1)$$

$$CR = (ED \times EF \times FIR \times MC \times CsFo) / (BW) \tag{2}$$

MCi denotes the concentration of HMs, expressed in milligrams per kilogram of wet weight. IR signifies the daily consumption of fishery catches, measured in grams. BW stands for body weight of an individual, with a standard assumption of 60 kilograms for adults and 30 kilograms for children. EF is defined as the number of days per year an individual is exposed to a certain substance, with a standard value of 365. At is the average lifespan (days, 25550 for adults and 4380 for children). RfD is a consult of the daily exposure to a substance (mg/kg/d: 3 for As, 0.5 for Cd, 3 for Cr, 40 for Cu, 11 for Ni, 140 for Mn, 3.5 for Pb, 3 00 for As), CsFo is carcinogenic slope factor (mg/kg/d: 1.5 for As, 0.5 for Cd, 6.3 for Cr, and 0.0085 for Pb). The acceptable limits for HMs were as follows: HQ < 1, acceptable; HQ >1, unacceptable;  $CR \leq 1 \times 10^{-6}$ , negligible;  $1 \times 10^{-6} < CR \leq 1 \times 10^{-4}$ , acceptable;  $1 \times 10^{-4} < CR$ , no acceptable.

Employing a prospective ecological risk assessment protocol, we evaluated the latent ecological hazards posed by HMs in the marine environment. Formula was as follows:

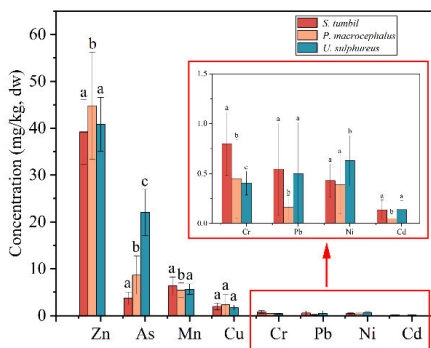
$$RI = \sum E_r^i = \sum T_r^i \times C_i / C_n^i \tag{3}$$

RI denotes the potential ecological risk index.  $E_n^i$  is the potential ecological risk coefficient attributed to HM.  $T_r^i$  is the toxicity index of HM, with specific values assigned to As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn as 10, 30, 2, 5, 40, 5, 5, and 1, correspondingly.  $C_i$  is the concentration of HM in surface sediment samples.  $C_n^i$  is the background value of HM. The criteria for HMs in sediments were as follows: RI <150, low ecological risk; 150 <RI <300, moderate ecological risk; 300 <RI <600, considerable ecological risk; RI >600, very high ecological risk.

### 3 Result and discussion

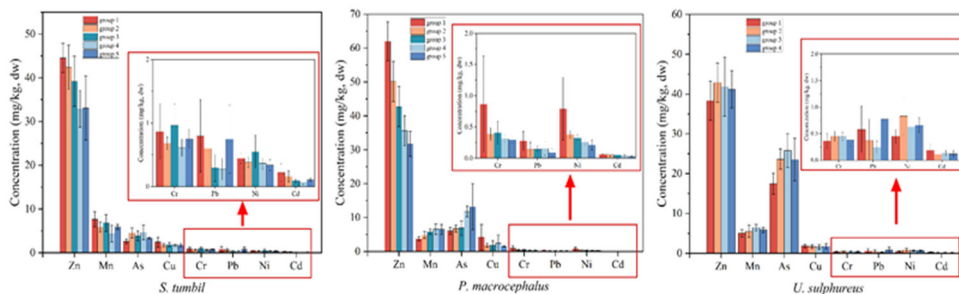
#### 3.1 HMs accumulation in fishery catches

The order of HM contents (mean ± standard deviation, mg/kg, dw) in fishery catches was: Zn (41.70 ± 8.91) > As (10.94 ± 8.38) > Cu (2.00 ± 1.459) > Mn (5.80 ± 1.63) > Cr (0.55 ± 0.359) > Ni (0.47 ± 0.269) > Pb (0.39 ± 0.43) > Cd (0.11 ± 0.089). ANOVA analysis revealed significant differences in As and Cr levels among the three fish species depicted in Figure 2, whereas Cu and Ni levels did not exhibit significant differences ( $P < 0.05$ ). Mn, Pb and Cd levels in *P.m.* were notably lower compared to *S. t.* and *U. s.*, except for Zn.. The disparity in HM bioconcentration among fishery catches investigated likely stems from distinct metal processing dynamics within these fish, compounded by their diverse dietary behaviors.



**Fig. 2.** Variations in the accumulation of HMs among fishery catches exhibit significant differences.

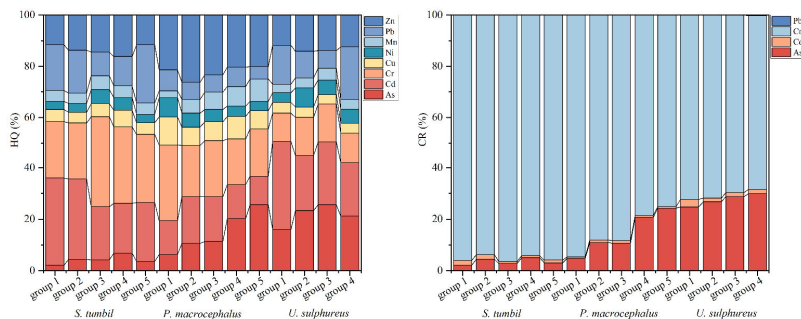
Figure 3 illustrates the levels of the 8 HMs across different length groups of *S. t.*, *P. m.* and *U. s.*. Concentrations (mg/kg) of Zn spanned a range, with the lowest levels detected at 31.71 in group 5 of *P. m.* and the highest at 61.98 mg/kg in group 1 of the same species, denoting a highly significant variation ( $P < 0.05$ ) associated with the distinct body length. Mn concentrations in the fish specimens under investigation varied between 3.69 in the first group of *P. m.* to a peak of 7.65 in the first group of *S.t.*. Notably, a statistically significant variation in As concentrations was detected between the groups of *S.t.* and *U.s.* suggesting potential As contamination in the body length category of *U.s.*



**Fig. 3.** HMs accumulation varies across different groups within the fishery catches.

### 3.2 Assessment of human health risks posed by HMs in fishery catches

For adults and children, HQ values of 8 HMs were  $<1$ . THQ values of the fishery catches consumed by adults also remained below 1. Conversely, for children, the THQ for *S.t.* (2.43), *P.m.* (1.7), *U.s.* (3.39) were  $>1$ , implying a potential risk of adverse health outcomes from the ingestion of metals present in fishery catches. The primary contributors to THQ in *S. t.* were Cr and Cd, with respective contributions of 25.60% and 27.43%, respectively (Figure 4). In *P.m.*, Zn and Cr were the most significant. Meanwhile, in *U.s.*, Cd and As were the leading factors, accounting for 25.61% and 21.52% of THQ. For adults, CR associated with HM intake from consuming the fishery catches was deemed acceptable. In children, excluding Cd and Pb, the CR values for As and Cr were notably above the acceptable bounds. Additionally, TCR for all fishery catches surpassed the safe intake levels for both age groups corroborating earlier findings that highlight the potential health hazards linked to seafood ingestion.



**Fig. 4.** Contribution rates of 8 HMs in fishery catches of THQ and TCR.

### 3.3 Ecological risk assessment of HMs in surface sediments

The K-S test showed that the investigated HMs were normally distributed or lognormally distributed. The overall sediment contents (mean ± standard deviation) of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn in the main bays of Guangxi were 13.38 ± 6.45, 0.058 ± 0.044, 31.83 ± 15.68, 13.71 ± 7.66, 0.024 ± 0.021, 13.18 ± 9.34, 24.24 ± 19.28 and 24.24 ± 0.021, respectively.

The range of 8 HMs reached China’s national first-class benchmark of marine sediment quality.  $E_r^I$  of HMs in the surface sediments of major bays in Guangxi was in the low-risk category (Table 2). RI of HMs in the surface sediments of main bays in Guangxi spanned between 17.77 and 133.88, averaging at 56.45, indicative of a slightly polluted state. The main sources of potential ecological risk were As, Cd and Hg, which contributed 27.17%, 29.42% and 22.78%, respectively.

**Table 2.** Potential ecological risk indices for HMs in the surface sediments of major bays in the Beibu Gulf.

Region		$E_r^I$								RI
		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	
ZhenZhu Bay	Max	1.98	1.95	0.46	1.24	1.21	0.54	0.43	0.09	17.77
	Min	16.53	21.52	1.24	3.59	18.63	2.40	5.51	0.53	53.25
	Mean	9.97	8.44	0.78	2.24	7.56	1.22	2.04	0.25	32.50
QingZhou Bay	Max	3.62	3.37	0.58	1.03	1.56	2.25	0.69	0.14	22.48
	Min	22.46	38.57	2.55	6.15	23.04	5.96	8.26	0.96	103.92
	Mean	13.28	22.32	1.42	4.13	15.05	4.43	5.68	0.56	66.88
LianZhou Bay	Max	3.30	7.39	0.43	0.94	8.00	0.48	2.38	0.25	34.86
	Min	22.57	49.92	1.76	5.93	48.14	5.49	12.78	1.17	133.88
	Mean	14.19	30.78	1.17	3.45	27.23	2.87	8.27	0.62	88.58
Mean		11.95	18.03	1.04	3.03	14.87	2.45	4.66	0.43	56.45
Contribution (%)		22.17	29.42	2.12	5.94	22.78	4.63	7.18	0.76	--

## 4 Conclusion

This study offered insights into the concentrations of 8 common HMs in fishery catches from the Beibu Gulf. It further evaluated the health hazards from consuming this seafood for adults and children, as well as ecological risks linked to HMs in the sediments of the major bays. The findings indicated significant variability in As and Cr levels. The human health risk revealed that children be at risk of both non-carcinogenic and carcinogenic hazards associated with HM intake. The results of RI revealed a low ecological risk from HMs in the surface sediments of the major bays of the Beibu Gulf, with Cd, As, and Hg being the primary elements contributing to the potential ecological risk of HMs in the sediments of the Beibu Gulf.

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