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EDITED BY
Peng Lin,
Texas A&M University at Galveston,
United States

REVIEWED BY
Ruifeng Zhang,
Shanghai Jiao Tong University, China
Fengxia Zhou,
Guangdong Ocean University, China

*CORRESPONDENCE
Zuhao Zhu
zhuzuhao@4io.org.cn

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Spatial and seasonal characteristics of dissolved heavy metals in the seawater of Beibu Gulf, the Northern South China Sea

Zuhao Zhu[1,2*], Huihua Wei[1], Yao Guan[1,2], Li Zhang[1,2], Pengfei Sun[1,2] and Qiufeng Zhang[2]

[1]Guangxi Key Laboratory of Beibu Gulf Marine Resources, Environment and Sustainable Development, Fourth Institute of Oceanography, Ministry of Natural Resources, Beihai, China, [2]Key Laboratory of Tropical Marine Ecosystem and Bioresource, Fourth Institute of Oceanography, Ministry of Natural Resources, Beihai, China

Heavy metal contaminations in the marine environment are of considerable attention because of their high potential ecological effects and public concern for human health. However, the influencing factors for the large-scale distributions of heavy metals in Beibu Gulf, a newly developing industry and port in South China, are still unclear due to the lack of large-scale investigation. Here, a total of 871 samples in the 127 stations in the seawater of Beibu Gulf during spring, summer, fall and winter in 2020-2021 were analyzed for dissolved heavy metal concentrations and physicochemical parameters. The concentrations of heavy metals in the Beibu Gulf ranked following the order of Zn > Cu > Cr > As > Pb > Hg > Cd. Compared to other regions, the concentrations of Hg were at relatively higher levels, which were mainly influenced by the input of the transportation of water masses from the local and other regions; whereas the other heavy metals were at relatively lower levels. Seasonally variations in the concentrations of heavy metals were observed in the gulf, which is mainly influenced by human activities (i.e., shipping and mariculture activities) and seasonally hydrological conditions. Seasonal changes in the spatial distribution of heavy metals have been found in the gulf. The higher concentrations of heavy metals mainly occurred in the coastal bays or areas in summer whereas the higher concentrations were observed in the offshore areas during the other three seasons. This is mainly related to the seasonal changes of the water masses that affect the seawater of Beibu Gulf, which exhibits the dominant contribution of coastal current from the northern Beibu Gulf in summer, and the dominant contribution of west-Guangdong coastal current and SCS water during the other three seasons. The potential ecological risk index revealed that Hg is the main ecological risk factor in the gulf, and the heavy metal contamination in the gulf seems to be noticeable. This study highlights the seasonal changes of the water masses that affect the seawater of Beibu Gulf greatly affecting the large-scale distributions of heavy metals in the gulf.

KEYWORDS

heavy metals, seasonal and spatial variation, water mass, ecological risk assessment, Beibu Gulf

Introduction

Since the 1950s, public hazard caused by heavy metal pollution, such as the mercury-caused Minamata disease in Japan and the occurrence of the cadmium Itaiitai disease, has been of great concern due to their persistence, high toxicity, non-degradability, and vast sources (Wang et al., 2013). Particularly in the marine environment, with the rapid economic and social development, large quantities of anthropogenic sources of heavy metals are discharged into the coastal environment, and those metals can be bioaccumulated by the marine organisms and biomagnified through the food chain, and ultimately endanger human health (Rainbow and Luoma, 2011; Kumar et al., 2019; Lao et al., 2019a; Liu et al., 2020; Huang et al., 2021). Thus, a better understanding of the current status of heavy metal contamination in marine ecosystems has a significant implication for the sustainable development of marine ecosystems, the seafood industry, and public concerns (Wang et al., 2013; Zhu and Zheng, 2017a; Zhu and Zheng, 2017b; Zhu and Zheng, 2018; Liu et al., 2020; Lao et al., 2022a).

Many researches have been increasingly concerned about the heavy metals in the marine environment. For example, increasing anthropogenic inputs of heavy metals into the seawater of mariculture areas have been reported due to the continuous expansion of the mariculture scale for the past decades (Wang et al., 2019; Liu et al., 2020; Lao et al., 2022a; Mohsen et al., 2022). Moreover, the coastal currents play an important role on the distribution of materials, and greatly impact on the local marine environment (Dong et al., 2012; Li et al., 2018; Lv et al., 2021; Hu et al., 2022; Lao et al., 2022b; Lao et al., 2022c). Once the heavy metals input into the seawater, they can transport along with ocean currents to other areas, resulting in the wide spread of heavy metals in the marine environment (Li et al., 2018). Environmental change, such as ocean acidification and seasonal hypoxia, could change heavy metal status in the marine environment (Atkinson et al., 2007; Chakraborty et al., 2016; Ma et al., 2016; Lao et al., 2019a; Lao et al., 2022a). For example, the decrease of pH value in the marine environment leads to the re-release of heavy metals from sediments into the overlying water with linkage variation of metal concentrations in seawater and sediment environment, resulting in the decrease of heavy metals in sediments and the increase in seawater (Lao et al., 2022a).

Beibu Gulf, located in the northwestern South China Sea (SCS), is a newly developing industry and port in South China (Lao et al., 2021a). Additionally, the gulf is an important mariculture base and one of the most important fishing grounds in China because of its high productivity and rich biological diversity (Liu et al., 2020; Xu et al., 2020; Xu et al., 2021; Chen et al., 2022a). This is mainly because there is a stable external nutrient input to the Beibu Gulf from different water masses to maintain marine production (Lao et al., 2021b; Lao et al., 2022c). However, the ecosystems of the Beibu Gulf, particularly in the northern coastal bays, are now facing many environmental issues (Kaiser et al., 2016; Lao et al., 2019a; Lao et al., 2021a; Lao et al., 2021b; Zhang et al., 2021a; Cai et al., 2022; Chen et al., 2022a), such as the aggravating seawater acidification (Lao et al., 2022a) and eutrophication over the past years due to intensive human activities (Lao et al., 2021b; Cai et al., 2022). In addition, heavy metal contaminations have also been widely reported in coastal areas or bays around the northern Beibu Gulf. For example, the contamination of heavy metals and other pollutants in both seawater and sediment showed an increasing trend in the northern coastal bays over the past decades (Chen et al., 2018; Lao et al., 2019a; Liu et al., 2020; Zhu et al., 2021; Zhang et al., 2021b; Lao et al., 2022a; Zhang et al., 2022a), which also increased the proportions of bioavailable metals in the environment of the gulf (Kang et al., 2017; Chen et al., 2022a). Moreover, the heavy metals in the coastal wetland sediment cores of the northern Beibu Gulf also exhibited an increasing trend from 1985 to 2008 (Gan et al., 2013). The pH value in the seawater decreased by 4.7% over the past two decades, which greatly impacts the distribution of heavy metals in the seawater and sediment (Lao et al., 2022a). According to the assessment of potential ecological risk index (ERI) (Hakanson, 1980), Hg is the dominant risk factor in the coastal bays of northern Beibu Gulf due to intensive human activities, such as mariculture, agricultural, shipping and industrial activities (Lao et al., 2019; Liu et al., 2020; Lao et al., 2022a). In addition, there are several water masses, namely the coastal current, SCS water, and West-Guangdong coastal current that affecting the seawater in the Beibu Gulf (Figure 1) (Lao et al., 2022c). These water masses will

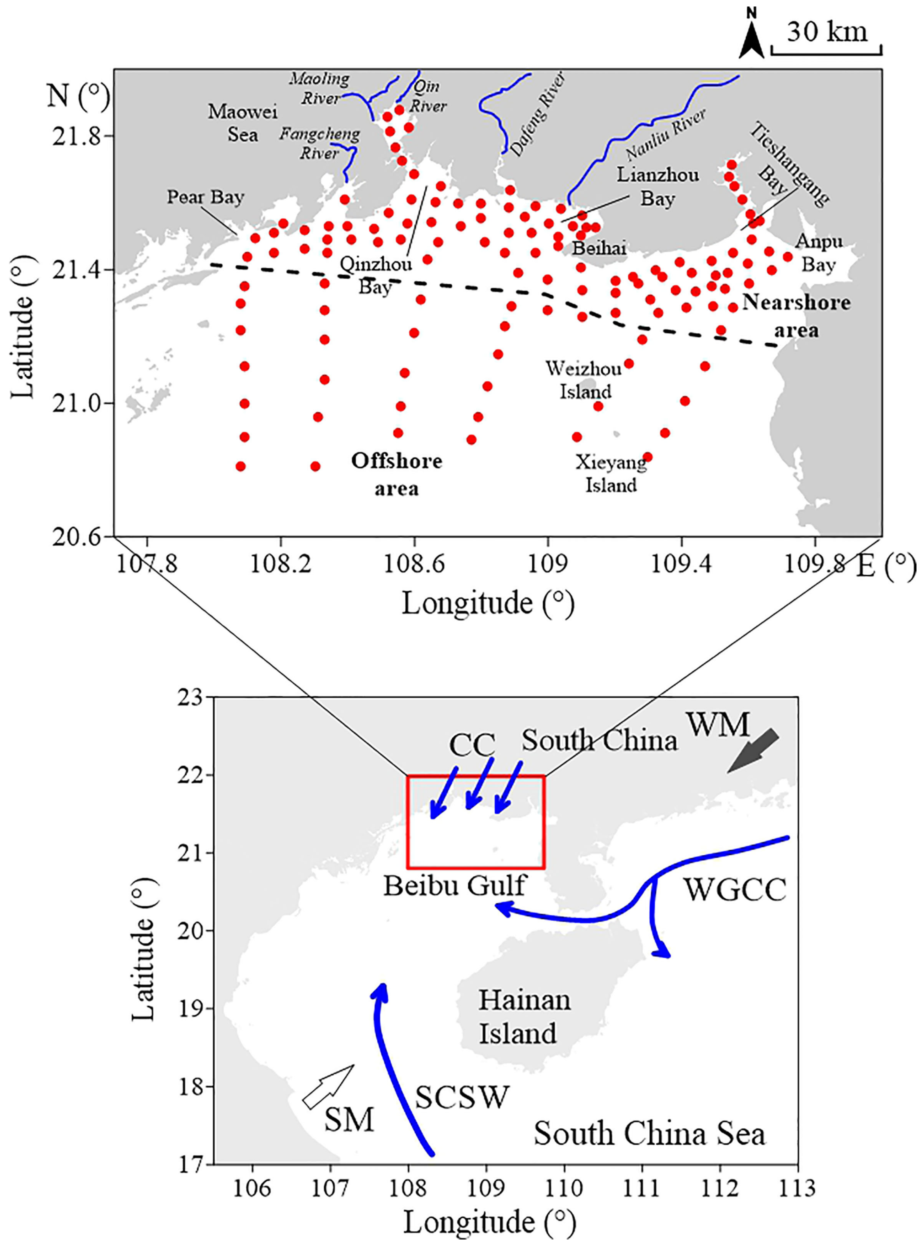

FIGURE 1
The study area and sampling sites (red blots) in Beibu Gulf. The dotted line is the dividing line between the nearshore and offshore area in the study area; the blue arrows in the below figure represent the water masses that affect the water in the gulf, which is modified from Lao et al. (2022c). WGCC, West-Guangdong coastal current; SCSW, South China Sea water; CC, coastal current from the Guangxi Province. The black and white arrows represent monsoons, SM, summer monsoon; WM, winter monsoon.

input rich materials into the Beibu Gulf (Chen et al., 2019; Lin et al., 2020; Lao et al., 2022c). Particularly the West-Guangdong coastal current, which originated from the diluted Pearl River and flows along the western coast of Guangdong Province with high contaminants into the Beibu Gulf through the Qiongzhou Strait (Chen et al., 2019; Lao et al., 2019b; Lin et al., 2020; Lao et al., 2022b; Lao et al., 2022c). However, the study on heavy metals in the Beibu Gulf is mainly on the nearshore or the coastal bays (Xia et al., 2011; Zhu and Zheng, 2013; Gu et al., 2015; Yang et al., 2015; Lao et al., 2019a; Liu et al., 2020; Yang et al., 2020; Lin et al., 2021; Lao et al., 2022a), and the characteristics of large-scale heavy metal contamination and distribution in the Beibu Gulf are still unclear. We speculate that the seasonal changes in water mass transportation in the

Beibu Gulf (Lao et al., 2022c) may have a great impact on the local heavy metal contaminations and distributions.

In this study, seasonal concentrations of seven heavy metals (Cu, Cd, Pb, Zn, As, Hg and Cr) and other physicochemical parameters in seawater in the large-scale Beibu Gulf were investigated to (1) analyze the seasonal distributions of heavy metals and their relationship with other related environmental parameters, (2) reveal the impact of seasonal intrusion of different water masses on the distribution of heavy metals and the possible behaviors and transition processes of those heavy metals in the gulf.

Materials and methods

Study area and sampling

The Beibu Gulf is a semi-enclosed bay with an average depth of 42 m and an area of about 130,000 km^2 located in the northwestern SCS. The gulf is surrounded by the coast of Guangxi Province in the north, Vietnam in the west, the Leizhou Peninsula in the east, and Hainan Island in the southeast (Figure 1). The west-Guangdong coastal current originates from the diluted Pearl River and flows along the coast of western Guangdong Province. After reaching the coastal area on the east side of Leizhou Peninsula, a tributary of the current enters into Beibu Gulf through Qiongzhou Strait. In addition, many rivers flow from the coast of Guangxi Province in the north into the northern coastal bays (e.g. Qinzhou Bay, Lianzhou Bay), with the higher runoff of the rivers in the rainy seasons (132.51×10^8 m^3) whereas lower runoff in the dry seasons (20.39×10^8 m^3) (Lao et al., 2020; Lao et al., 2022c). The runoff in the northern Beibu Gulf formed a coastal current that affects the seawater in the gulf, which become the dominant contributor to the seawater of the gulf in the rainy season (43% in summer and 45% in fall) due to the high runoff in the northern gulf during these periods (Lao et al., 2020; Lao et al., 2022c), while the dominant contributor to the seawater of the gulf changed to the intrusion of SCS water (57%) with high salinity through the coast of western Hainan Island during the dry season (winter) due to sharp drop of runoff (Lao et al., 2020; Lao et al., 2022c). However, the contribution of the west-Guangdong coastal current to the seawater of Beibu Gulf was relatively stable throughout the year (24-31%) (Lao et al., 2022c). Beibu Gulf is influenced by the East Asian monsoon, with the southwestern monsoons prevailing in summer and the northeastern monsoons prevailing in winter. The annual rainfall in the gulf is 1775 mm, with the dominant precipitation in the rainy season (April-October, 1579 mm) due to a large amount of rainfall brought by frequent typhoons and high rainfall frequency during this period (Chen et al., 2021; Luo et al., 2022). In this study, the study area is covering all northern Beibu Gulf, including the coastal bays in the north and the offshore area extending to the central gulf (Figure 1).

Four cruises were conducted during summer (July 2020), fall (September 2020), winter (January 2021), and spring (May 2021) in the Beibu Gulf. A total of 127 stations were set up in each season. Only surface water was collected when the depth is less than 10 m, and surface and bottom water were collected when the depth is greater than 10 m. A total of 217, 221, 215, and 208 seawater samples were collected using a rosette sampler fitted with 10 L Niskin bottles (Acid cleaned using 25% trace metal grade HNO_3) during spring, summer, fall, and winter, respectively. The profiles of salinity, temperature, and depth were determined using a calibrated Sea-Bird 911/19 plus CTD unit (USA). The seawater samples for total suspended particulate matter (TSM) were filtered by pre-weighed mix cellulose membranes (47 mm diameter and 0.45 µm pore size). The dissolved oxygen (DO) and pH were measured on-site using a calibrated multi-parameter water quality analyzer (Proplus, YSI, USA). The seawater samples for heavy metals were filtered using acid-cleaned cellulose acetate filters (47 mm diameter and 0.45 µm pore size, Entegris, China), and the filtrate was transferred into an acid-cleaned polyethylene bottle (250 mL), and then added HNO_3 (Trace metal grade, CNW, Germany) to the filtrate to achieve a pH<2. The filtrate of the heavy metal sample was stored at -20°C until analysis.

Sample analysis

The seawater samples for the analysis of Cu, Pb, Zn, Cd, and Cr concentrations were diluted 20-fold using 2% HNO_3 and then determined using an inductively coupled plasma mass spectrometer (ICPMS, ThermoFisher iCAP RQ, Bremen, Germany) by external calibration method. The samples for the analysis of As were pretreated with HCl (Trace metal grade, CNW, Germany) and thiourea-anticyclic acid (GR, Sinopharm, China) reducing agent for 30min. The samples for Hg were digested with sulfuric acid potassium persulfate (GR, Sinopharm, China) for 24 hours and then added with hydroxylamine hydrochloride (GR, Sinopharm, China) solution. The concentrations of As and Hg were determined using an atomic fluorescence spectrophotometer (AFS, Haiguang HGF-V2, Beijing, China) by an external calibration method. The method detection limits (Detailed in the supplementary materials) of Cr, Cu, Pb, Zn, Cd, Hg and As were 0.004 µg L^{-1}, 0.003 µg L^{-1}, 0.008 µg L^{-1}, 0.005 µg L^{-1} and 0.001 µg L^{-1}, 0.001 µg L^{-1}, 0.01 µg L^{-1}, respectively.

Quality control

Milli-Q water and trace metal-grade ultra-pure acids were used throughout the analysis. All labware was soaked with nitric acid (25%) for 7d and then cleaned with Milli-Q water before use. Procedure blanks were prepared by filtrating Milli-Q water and acidified to pH< 2 during the cruises. To ensure high precision and accuracy, blanks, duplicate samples, and certified reference materials (CRMs) were prepared with each batch of test samples (20 samples a batch). Seawater trace metal CRM GBW(E)080040 (For Cr, Cu, Pb, Zn, Cd, Second Institute of Oceanography, Ministry of Natural Resources, Hangzhou, China) was used for ICPMS analysis validation, CRM GBW(E) 080042 (For Hg, Second Institute of Oceanography, Ministry of Natural Resources, Hangzhou, China) and CASS-5 (For As, National Research Council Canada, Ottawa, Canada) was used for AFS analysis validation. The relative standard deviation (RSD) of the determination methods was< 6%, and the recoveries were ± 10%, further analytical figures of merit were detailed in the supplementary materials. The metal concentrations were all blank-corrected in this study.

Heavy metal pollution assessment

The ERI proposed by Hakanson (1980) was used to conduct the risk assessment of heavy metal pollution in seawater of the Beibu Gulf. This method not only takes into account the heavy metal pollution coefficient obtained by the single factor pollution index method, but also introduces the toxicological response coefficient of heavy metals. The calculation formula of the ERI is as follows:

$$\mathrm{ERI} = \sum_{i=1}^{N} E_r^i = \sum_{i=1}^{N} T_f^i \times \frac{C_i}{C_o} \quad (1)$$

where C_i and C_o denote the measured value of a heavy metal element in seawater (both surface and bottom water samples) and a standard value, T_f^i denotes toxic response factor (TRF), E_r^i denotes each metal potential ERI. In this study, C_o obtained from the National Standard of China for Seawater Quality GB 3097-1997, Grades I, and T_f^i of Hg, As, Cr, Cu, Pb, Zn, and Cd were 40, 10, 2, 5, 5, 1, and 30 (Liu et al., 2020; Lao et al., 2022a). To assess the potential ecological risk, the ERI could be classified into five grades (Table 1) (Liu et al., 2020; Lao et al., 2022a).

Statistical analysis

The data in this study were statistically analyzed by the IBM SPSS Statistics (Version 19.0). The spatial distributions of heavy metals were formed using Ocean Data View (Version 4.0). The analysis of Student's *t*-test of the difference between the parameters in the two groups were performed using the IBM SPSS Statistics (Version 19.0). The correlations analysis and principal component analysis (PCA) between metals and other environmental factors were also performed by the IBM SPSS Statistics (Version 19.0). Notably, One-way ANOVA was carried out to verify whether the data had homogeneous variances (F-test) before the application of Student's t-test.

Results

Physicochemical parameters in the Beibu Gulf

The physicochemical parameters in the seawater during the four seasons were illustrated in Figure 2. The temperature ranged from 12.70 to 33.70 °C. The salinity varied greatly in the gulf, and the values ranged from 2.20 to 34.21, with higher salinity in the dry seasons (winter (an average of 31.00) > fall (an average of 29.94), *t*-test, $p< 0.001$) and lower salinity in the rainy seasons (spring (an average of 27.56) > summer (an average of 26.94), *t*-test, $p< 0.01$) (Figure 2). The DO levels ranged from 3.40 to 10.30 mg L^{-1}, with a decreased level of winter > fall > spring > summer (*t*-test, all $p<$ 0.001). The pH values ranged from 7.46 to 8.90. The concentrations of TSM varied greatly with seasons, and the concentrations ranged from 0.01 to 99.32 mg L^{-1}, with a decreased concentration of fall > summer > winter > spring (*t*-test, all $p< 0.001$).

Heavy metals in the seawater of Beibu Gulf

The concentrations of the seven heavy metals in the Beibu Gulf during the four seasons were presented in Table 2. The seasonal variations of heavy metals in Beibu Gulf were presented in Figure 3.

TABLE 1 The relationship between ecological risk index and pollution degree.

E_r^i	ERI	Pollution level
$E_r^i<40$	ERI<150	Low ecological risk
$40\le E_r^i<80$	150≤ERI<300	Moderate ecological risk
$80\le E_r^i<160$	300≤ERI<600	High ecological risk
$160\le E_r^i<320$		Very high ecological risk
$E_r^i\ge 320$	ERI≥600	Extremely high ecological risk

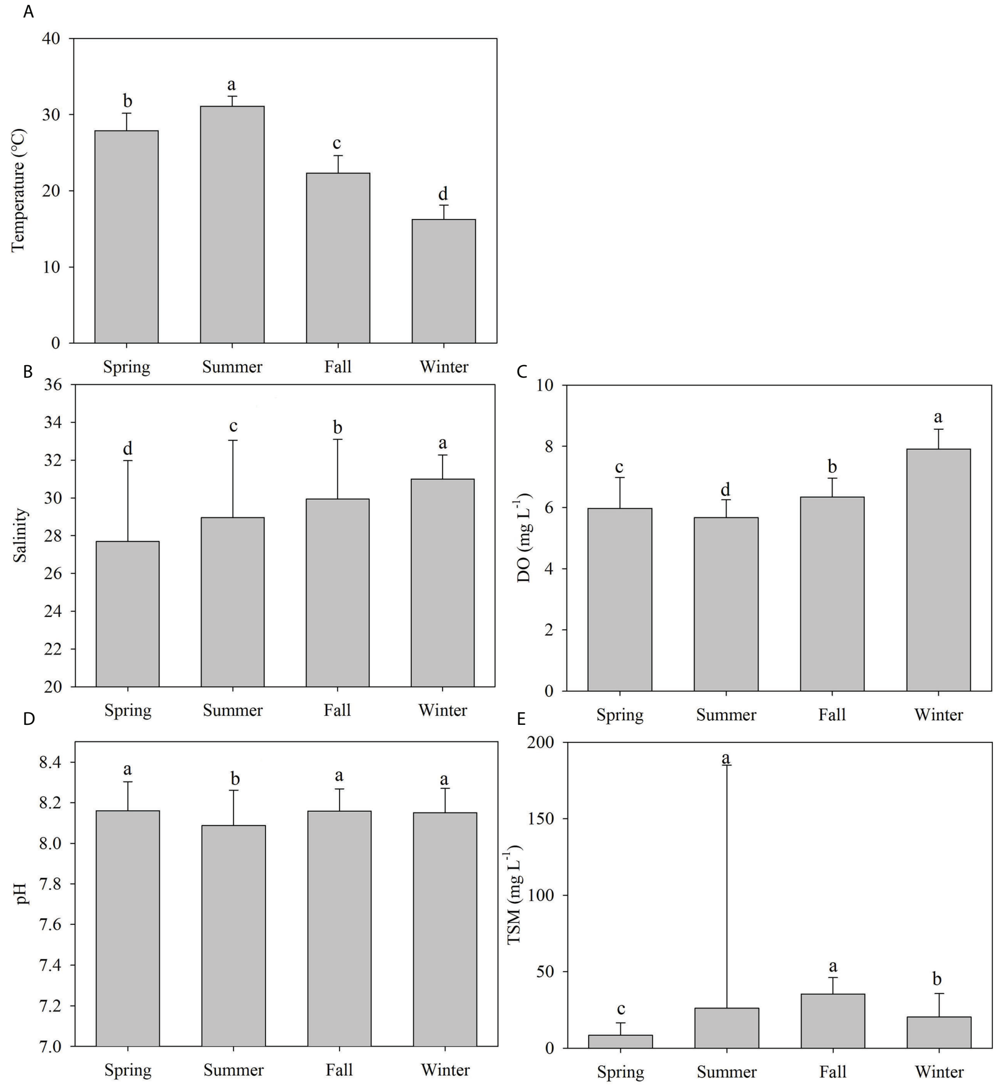

FIGURE 2
Seasonal variations of physicochemical parameters in the seawater of Beibu Gulf. The same letters in the bar chart denote significant differences; different letters in the bar chart denote significant differences. **(A)** Temperature; **(B)** Salinity; **(C)** DO; **(D)** pH; **(E)** TSM.

The concentrations of Cr, Cu, Cd, Pb, Zn, As, and Hg in the whole Beibu Gulf (both surface and bottom water) during the four seasons ranged from not detected (ND) to 6.81 μg L^{-1}, ND to 7.74 μg L^{-1}, ND to 0.26 μg L^{-1}, ND to 5.77 μg L^{-1}, ND to 74.87 μg L^{-1}, ND to 1.18 μg L^{-1} and ND to 0.36 μg L^{-1}, respectively, which ranked following the order of Zn (12.12 μg L^{-1}) > Cu (1.06 μg L^{-1}) > Cr (0.65 μg L^{-1}) > As (0.62 μg L^{-1}) > Pb (0.23 μg L^{-1}) > Hg (0.08 μg L^{-1}) > Cd (0.03 μg L^{-1}). The seasonal variations of heavy metals are quite different in the gulf (Figure 3 and Table 2). Generally, the concentrations of Cr, Cd, Zn in winter and spring were significantly higher than that in summer (*t*-test, all $p< 0.001$) and fall (*t*-test, all $p< 0.001$). By contrast, concentrations of Cu, As and Hg in summer were significantly higher than that in the other three seasons (*t*-test, all $p< 0.05$). The concentrations of Pb in winter were significantly higher than in other seasons (*t*-test, all $p< 0.001$). The seasonal variation of different heavy metal concentrations indicates that their sources and factors affecting their distribution could be different. Spatially, the higher concentrations of Cu in summer were observed in the northern coastal bays (*t*-test, all $p< 0.01$) (Figure 4B), whereas the higher concentrations in other seasons were observed in the offshore areas (*t*-test, all $p< 0.01$). The higher concentrations of Pb were observed in the offshore areas during fall (*t*-test, $p< 0.001$) (Figure 4G) and winter (*t*-test, $p< 0.01$) (Figure 4F). However, the concentrations of Pb were lower in the gulf during spring and summer (*t*-test, all $p< 0.01$) except for a higher concentration in Weizhou Island during spring and in the

TABLE 2 Concentrations of heavy metals in seawater of the Beibu Gulf during different seasons (μg L^{-1}).

Heavy metal		Spring		Summer		Autumn		Winter	
		Range	Average	Range	Average	Range	Average	Range	Average
Cu	Surface	0.46-4.66	1.04 ± 0.51	0.32-4.82	1.54 ± 0.90	0.10-4.68	0.90 ± 0.61	0.06-5.88	1.00 ± 0.79
	Bottom	0.30-3.28	0.94 ± 0.48	0.30-5.79	1.11 ± 0.85	ND-7.53	0.93 ± 1.07	0.10-7.74	0.96 ± 1.00
	All	0.30-4.66	1.00 ± 0.50	0.30-5.79	1.36 ± 0.90	ND-7.53	0.91 ± 0.83	0.06-7.74	1.56 ± 6.00
Pb	Surface	ND-1.58	0.10 ± 0.19	ND-5.77	0.21 ± 0.63	ND-2.64	0.25 ± 0.35	0.04-3.32	0.51 ± 0.62
	Bottom	ND-0.34	0.08 ± 0.07	ND-0.56	0.11 ± 0.12	ND-2.01	0.24 ± 0.34	0.04-2.49	0.45 ± 0.47
	All	ND-1.58	0.09 ± 0.16	ND-5.77	0.17 ± 0.49	ND-2.64	0.40 ± 2.12	0.04-3.32	0.57 ± 0.96
Zn	Surface	0.50-32.62	15.63 ± 4.92	ND-44.24	5.84 ± 10.22	0.18-63.60	15.66 ± 9.26	2.64-74.87	16.38 ± 11.98
	Bottom	0.54-28.02	15.35 ± 5.48	ND-47.54	2.86 ± 7.90	0.02-42.44	8.08 ± 9.03	2.50-58.90	14.74 ± 9.84
	All	0.50-32.62	15.51 ± 5.16	ND-47.54	4.60 ± 9.44	0.02-63.60	12.56 ± 9.90	2.50-74.85	15.70 ± 11.16
Cd	Surface	0.02-0.08	0.03 ± 0.01	ND-0.10	0.03 ± 0.02	ND-0.06	0.03 ± 0.01	ND-0.26	0.03 ± 0.03
	Bottom	0.02-0.08	0.03 ± 0.01	ND-0.11	0.02 ± 0.01	ND-0.13	0.02 ± 0.02	ND-0.07	0.02 ± .0.01
	All	0.02-0.08	0.03 ± 0.01	ND-0.11	0.03 ± 0.02	ND-0.13	0.02 ± 0.01	ND ~0.26	0.03 ± 0.02
Cr	Surface	0.16-1.82	0.67 ± 0.27	0.15-2.00	0.55 ± 0.26	0.14-4.03	0.49 ± 0.56	0.11-4.86	0.88 ± 0.78
	Bottom	0.08-5.06	0.77 ± 0.63	0.21-1.09	0.51 ± 0.18	0.01-6.76	0.50 ± 0.80	ND-6.81	0.81 ± 1.00
	All	0.08-5.06	0.71 ± 0.46	0.15-2.00	0.53 ± 0.23	0.01-6.76	0.50 ± 0.67	ND-6.81	0.85 ± 0.88
As	Surface	0.33-1.18	0.67 ± 0.16	0.29-1.11	0.69 ± 0.15	0.21-1.03	0.64 ± 0.14	0.18-0.77	0.46 ± 0.15
	Bottom	0.33-0.99	0.71 ± 0.14	0.40-0.95	0.70 ± 0.12	0.28-0.87	0.64 ± 0.12	ND-0.76	0.49 ± 0.15
	All	0.33-1.18	0.68 ± 0.15	0.29-1.11	0.70 ± 0.14	0.21-1.03	0.64 ± 0.13	ND-0.77	0.48 ± 0.15
Hg	Surface	ND-0.31	0.07 ± 0.04	0.01-0.29	0.10 ± 0.05	ND-0.15	0.06 ± 0.02	ND-0.17	0.06 ± 0.02
	Bottom	ND-0.36	0.08 ± 0.05	0.01-0.33	0.12 ± 0.07	0.02-0.16	0.07 ± 0.02	0.03-0.09	0.06 ± 0.02
	All	ND-0.36	0.08 ± 0.05	0.01-0.33	0.11 ± 0.06	ND-0.16	0.07 ± 0.02	0.02-0.17	0.06 ± 0.02

nearshore of the central gulf during summer (Figures 4E, F). The higher concentrations of Zn were all observed in the offshore area during spring (*t*-test, $p< 0.01$), fall (*t*-test, $p< 0.01$) and winter (*t*-test, $p< 0.01$), while the higher concentrations were observed in the nearshore during summer (*t*-test, $p< 0.001$) (Figures 5A–D). The higher concentrations of Cd were generally observed in the nearshore areas during the four seasons (*t*-test, all $p< 0.05$) (Figures 5E–H). Significantly higher concentrations of Hg occurred in the offshore areas during summer (*t*-test, $p< 0.001$) (Figure 6B), whereas slightly higher concentrations occurred in the coastal bays during fall (*t*-test, $p< 0.01$) (Figure 6C). The higher concentrations of As during spring, summer, and fall were all observed in Tieshangang Bay and Lianzhou bay (Figure 6), whereas the higher concentrations were observed in the offshore areas during winter (*t*-test, $p< 0.001$) (Figure 6H). The concentrations of Cr were generally lower in the coastal bays during the four seasons, whereas higher concentrations occurred in the offshore areas, particularly in the fall (*t*-test, $p< 0.001$) and winter (*t*-test, $p< 0.001$) (Figure 7).

The relationship between heavy metals and other physicochemical parameters

The correlation analysis between the physicochemical parameters and heavy metals were presented in Table 3. The seven heavy metals are all related to physicochemical factors. The concentrations of Cu and Hg are positively correlated with temperature but negatively correlated with DO. In addition, the concentrations of Cu are also negatively correlated with salinity and pH. The concentrations of Cr are positively correlated with DO. The concentrations of Cd and As are negatively correlated with salinity, DO, and pH. The concentrations of Cu and As are positively correlated with TSM, but the concentrations of Hg are negatively correlated with TSM. The concentrations of Pb and Zn are positively correlated with DO but negatively correlated with temperature. In addition, the concentrations of Pb are also positively correlated with salinity.

Assessment of heavy metal contamination in the seawater

The calculated potential ERI E_r^i for each heavy metal and the ERI are presented in Table 6. During the whole year, the E_r^i values decreased in the order of Hg > Pb > Cu > Cd > Zn > As > Cr. The contribution of Hg for ERI is 94% to be the main ecological risk factor in the Beibu Gulf, and which is similar to the previous studies on the coast of the northern Beibu Gulf (Liu et al., 2020; Lao et al., 2022a). Seasonally, the highest ERI was found in summer, followed by spring, fall, and the lowest value was found in winter (Table 4). Similarly, Hg is the main ecological

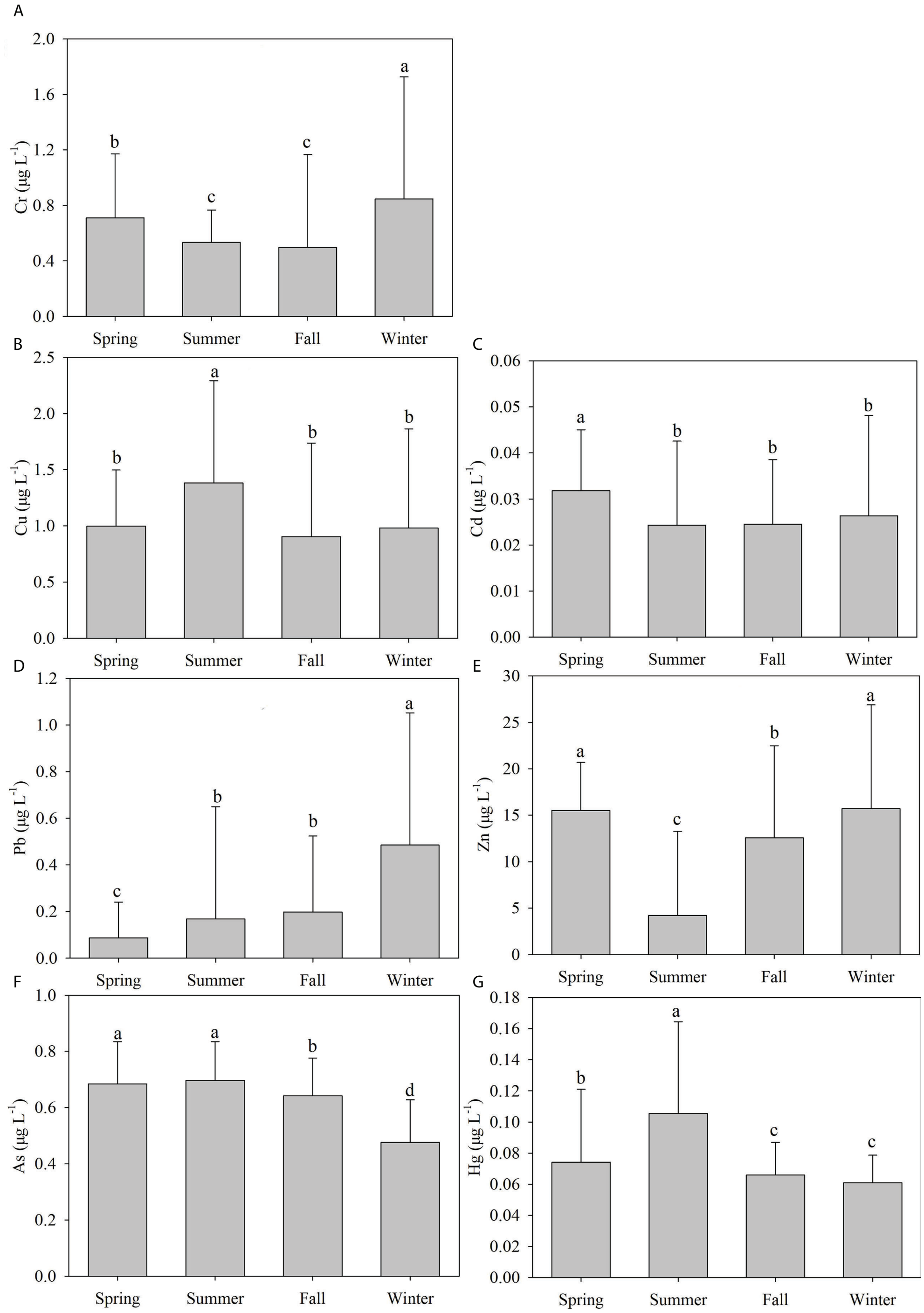

FIGURE 3
Seasonal variations of heavy metals in the seawater (including both surface and bottom) of Beibu Gulf. The same letters in the bar chart denote significant differences; different letters in the bar chart denote significant differences. **(A)** Cr; **(B)** Cu; **(C)** Cd; **(D)** Pb; **(E)** Zn; **(F)** As; **(G)** Hg.

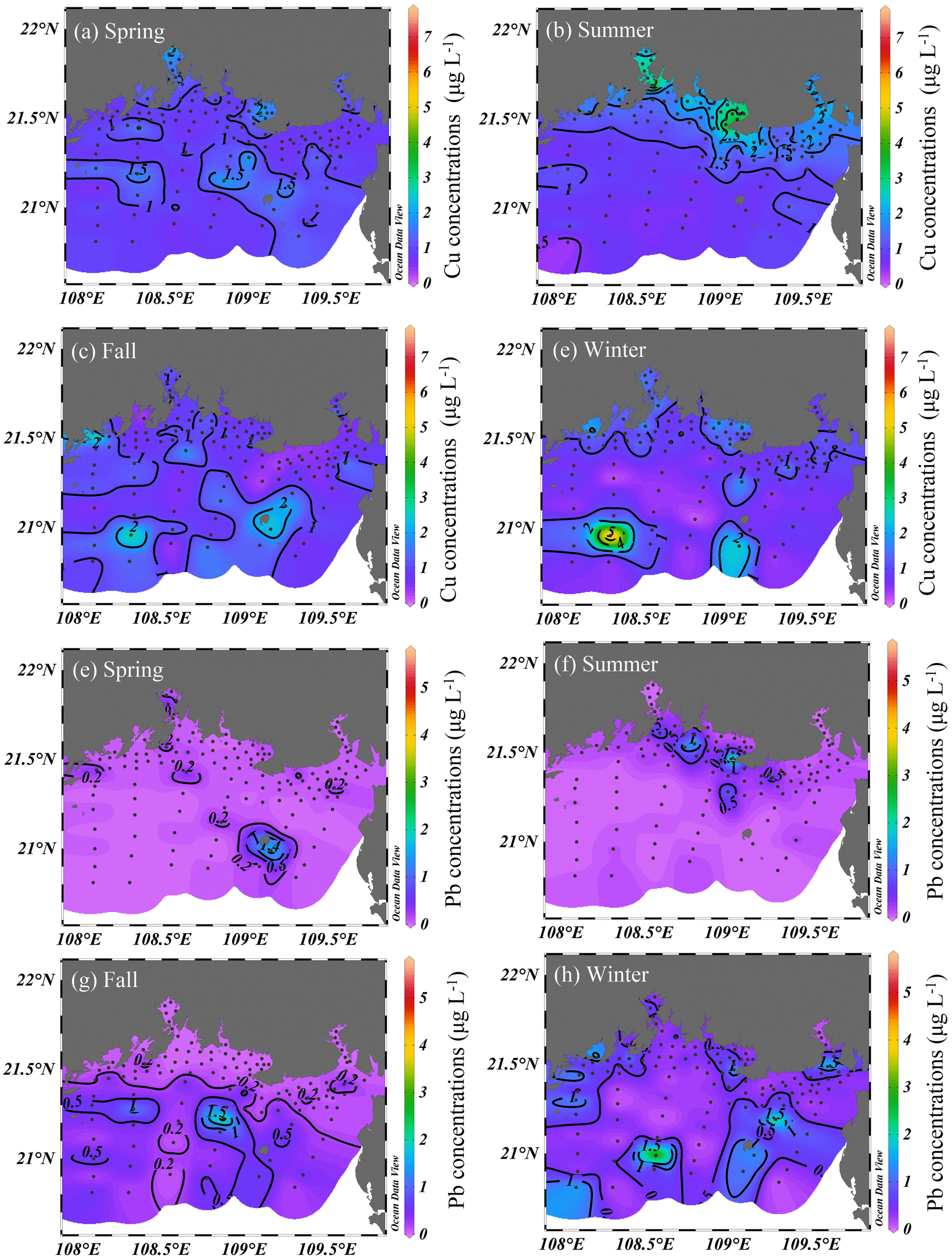

FIGURE 4
Spatial distributions of Cu and Pb in the surface seawater of Beibu Gulf during the sampling periods. **(A)** Cu-Spring; **(B)** Cu-Summer; **(C)** Cu-Fall; **(D)** Cu-Winter; **(E)** Pb-Spring; **(F)** Pb-Summer; **(G)** Pb-Fall; **(H)**-Pb-Winter.

risk factor during the four seasons. Moreover, the E_r^i values for Hg in the four seasons were all higher than 40, and the contribution for ERI in spring, summer, fall and winter were 95%, 96%, 93% and 88%, respectively. This suggests that the higher potential ecological risk from Hg occurs in the Beibu Gulf, and the heavy metal contamination of Hg in the gulf seems to be noticeable.

Discussion

Contaminated characteristics of heavy metals in seawater of Beibu Gulf

According to the National Standard of China for Seawater Quality (NSCSQ, GB 3097-1997), the concentrations of Cr, Cu,

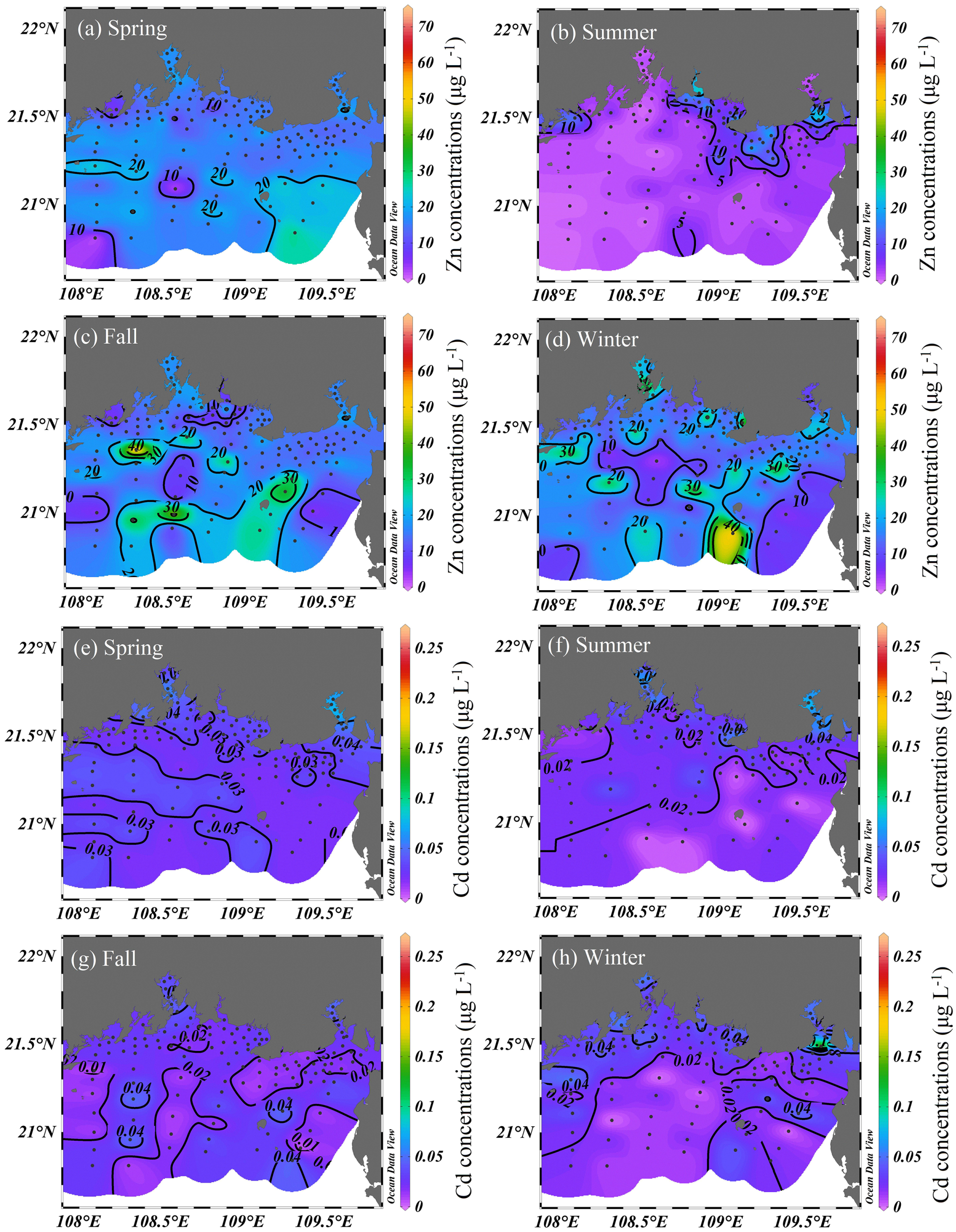

FIGURE 5
Spatial distributions of Zn and Cd in the surface seawater of Beibu Gulf during the sampling periods. **(A)** Zn-Spring; **(B)** Zn-Summer; **(C)** Zn-Fall; **(D)** Zn-Winter; **(E)** Cd-Spring; **(F)** Cd-Summer; **(G)** Cd-Fall; **(H)** Cd-Winter.

Cd, and As in the seawater of Beibu Gulf were all lower than the Grade I of NSCSQ (Table 4), suggesting that those heavy metals in the seawater of Beibu Gulf did not suffer from serious heavy metal contaminations. However, 0.5% of Pb and 18% of Zn concentrations exceed this standard, but the concentrations of those heavy metals were lower than the Grade II of NSCSQ. In addition, 84% of Hg concentrations were higher than the Grade I of NSCSQ, and there were still 4% of Hg concentrations higher than the Grade II of NSCSQ (Table 4). This indicates that Hg is the main contaminated metal in the seawater of Beibu Gulf.

Compared with other regions, the concentrations of heavy metals in the seawater of Beibu Gulf were either lower than or comparable with those of other similar regions, except for Hg

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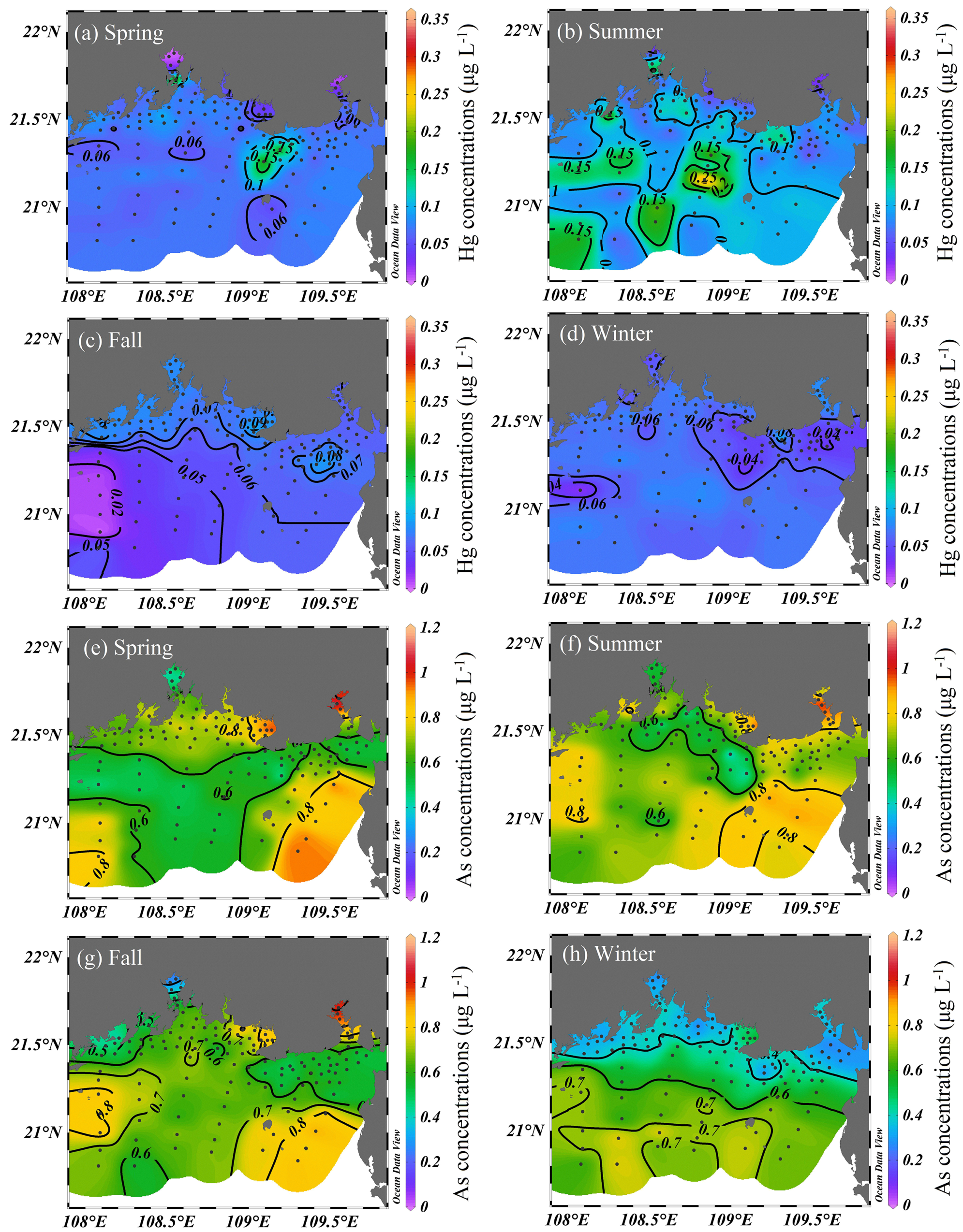

FIGURE 6
Spatial distributions of Hg and As in the surface seawater of Beibu Gulf during the sampling periods. **(A)** Hg-Spring; **(B)** Hg-Summer; **(C)** Hg-Fall; **(D)** Hg-Winter; **(E)** As-Spring; **(F)** As-Summer; **(G)** As-Fall; **(H)** As-Winter.

(Table 5). The concentrations of Hg were slightly lower than that in Liaodong Bay (Zhang et al., 2017), but higher than those other regions, such as 2.7 times higher than that in Jiaozhou Bay (Wang et al., 2012), 1.6 times higher than that in the Dingzi Bay and 1.3 times higher than that in the Xiangshan Bay (Zhao et al., 2018). This suggests that Hg is at a relatively high level in the seawater of Beibu Gulf. Similar to Liaodong Bay (Zhang et al., 2017), the rapid development of industry and intensive human activities could be responsible for the higher Hg contamination in the Beibu Gulf (Lao et al., 2019a; Liu et al., 2020). This is similar to the previous studies in the northern Beibu Gulf, which suggest that Hg is the main ecological risk factor in the gulf (Lao et al., 2019a; Liu et al., 2020; Lao et al., 2022a). The concentrations of Cu, Cd, and As in Beibu Gulf were generally lower than in other regions. The concentrations of Zn were lower than those in Liaodong Bay (Zhang et al., 2017), Dingzi

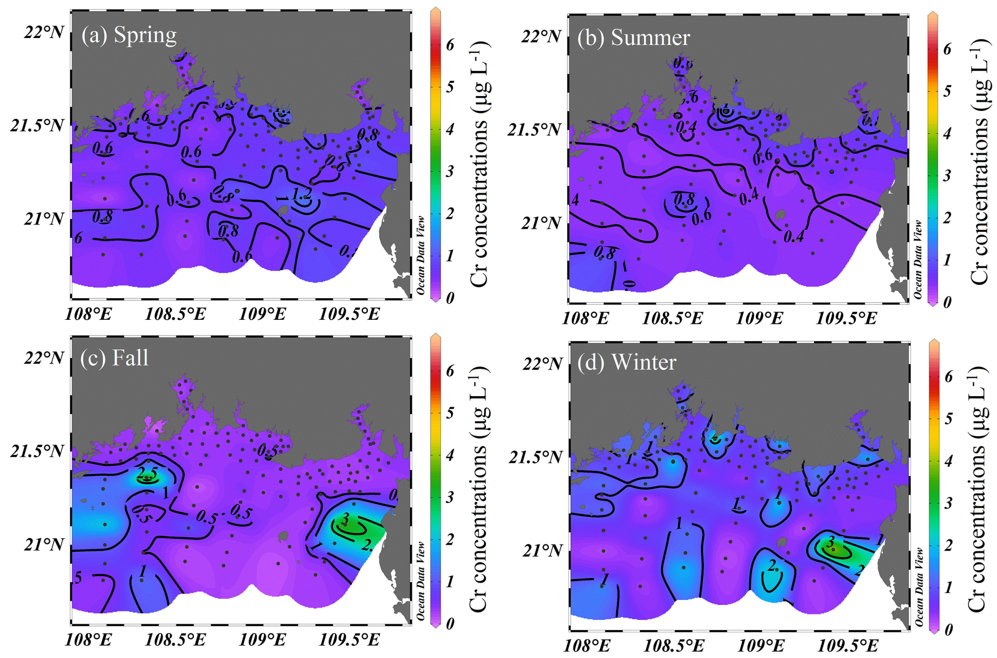

FIGURE 7
Spatial distributions of Cr in the surface seawater of Beibu Gulf during the sampling periods. **(A)** Cr-Spring; **(B)** Cr-Summer; **(C)**-Cr-Fall; **(D)** Cr-Winter.

Bay (Pan et al., 2014), Xiangshan Bay (Zhao et al., 2018), East Guangdong coastal area (Zhang et al., 2015) and Daya Bay (Qiu et al., 2005), but higher than those in Laoshan Bay (Wang et al., 2019) and Pearl River (Zhen et al., 2016). The concentrations of Cr were higher than that in Xiangshan Bay (Zhao et al., 2018), while the concentrations were lower than those in other regions. Although Zn, Cu and Cd in the seawater of coastal northern Beibu Gulf showed an increasing trend over the past two decades, the levels of those metals were still lower than in other relatively developed coastal bays (Lao et al., 2019a; Lao et al., 2022a). This may be related to the late beginning of the rapid development period of the coastal cities around the Beibu Gulf compared to the developed regions (Liu, 2020). The concentrations of Pb were comparable with Zhanjiang Bay (Zhang et al., 2018), but higher than the world average value (Gaillardet et al., 2005). Similar to the Zhanjiang Bay, Beibu Gulf is also a famous mariculture base in China, and the Pb concentrations showed an increasing trend over the past

TABLE 3 Correlation analysis between heavy metals and other physicochemical parameters in the Beibu Gulf.

	T	S	DO	pH	TSM	Cr	Cu	Cd	Pb	Zn	As	Hg
T	1	-0.25**	-0.34**	-0.13**	-0.01	-0.04	0.08**	-0.03	-0.12**	-0.14**	0.18**	0.20**
S		1	0.33**	0.56**	-0.06*	0.02	-0.22**	-0.29**	0.15**	0.00	-0.05	0.05
DO			1	0.40**	-0.14**	0.11**	-0.23**	-0.10**	0.25**	0.20**	-0.55**	-0.18**
pH				1	-0.08**	-0.02	-0.29**	-0.31**	0.04	0.03	-0.09**	0.03
TSM					1	0.03	0.09**	-0.05	0.03	-0.03	0.08**	-0.06*
Cr						1	0.24**	0.18**	0.24**	0.19**	-0.08**	-0.10**
Cu							1	0.32**	0.22**	0.19**	0.06*	-0.04
Cd								1	0.22**	0.19**	0.01	-0.11**
Pb									1	0.23**	-0.18**	-0.11**
Zn										1	-0.13**	-0.23**
As											1	0.11**
Hg												1

*Correlation is significant at the 0.01 level; **Correlation is significant at the 0.05 level.

TABLE 4 Potential ecological risk index of heavy metals in seawater of Beibu Gulf.

Time	E_r^i							ERI
	Cu	Pb	Zn	Cd	Cr	As	Hg	
Spring	1.00	0.45	0.78	0.9	0.03	0.34	64.00	67.5
Summer	1.36	0.85	0.23	0.9	0.02	0.35	88.00	91.71
Fall	0.91	2.00	0.63	0.6	0.02	0.32	56.00	60.48
Winter	1.56	2.85	0.79	0.9	0.03	0.24	48.00	54.37
annual	1.06	1.25	0.62	0.9	0.03	0.31	64.00	68.17

decades due to the rapid development of mariculture in the gulf (Liu et al., 2020; Lao et al., 2022a).

The biological and hydrodynamic influence on the distribution of heavy metals in the Beibu Gulf

The distribution and transport of heavy metals are greatly influenced by environmental factors and hydrological conditions (Chakraborty et al., 2016; Lao et al., 2019a; Wang et al., 2019; Lao et al., 2022a). The correlations and possible origins of heavy metals in the seawater of Beibu Gulf are further analyzed by PCA (Table 6). The values can explain 57.37% of the total heavy metals during the sampling period. In particular, PC1, PC2, PC3, and PC4 can explain 21.04%, 17.71%, 9.57%, and 9.50% of the total variance, respectively. High negative loadings for Cu, Cd, salinity, DO and pH were observed in the PC1, suggesting that those heavy metals are not only influenced by the terrestrial input but also influenced by biological activities. High positive loadings for Cr, Cu, Cd, Pb, and Zn in the PC2 indicated similar sources of those heavy metals. High positive loadings for salinity, Cr, Pb, and As were observed in the PC3, indicating that distributions of those heavy metals in the seawater of Beibu Gulf were mainly influenced by the transport of water masses with high salinity water from other areas. High negative loadings for TSM and Hg were observed in PC4, indicating the distribution of Hg was mainly influenced by the TSM in the seawater. Previous studies suggested that TSM is an important parameter that affects the distributions of dissolved heavy metals in the seawater (Feng et al., 2017; Zhang et al., 2018; Lao et al., 2019a; Lao et al., 2022a). However, the adsorption and desorption of heavy metals by particles in the seawater depend on the changes in the water environment, such as salinity, pH, and concentration of suspended particles (Lao et al., 2022a). For example, heavy metals would be more easily adsorbed onto the particles under higher salinity and TSM concentrations in the estuary areas (Feng et al., 2017), while the decrease of pH value would be more easily re-released from the particles to the seawater (Lao et al., 2022a).

Cu and Cd showed negative correlation with salinity, suggesting that those metals in the seawater of Beibu Gulf are mainly influenced by the terrestrial input. The higher concentrations of Cu and Cd were mainly observed in the

TABLE 5 Comparison of concentrations of heavy metals (μg L^{-1}) in seawater of Beibu Gulf with other regions.

Area	period	Hg	Cu	Pb	Cd	Zn	Cr	As	Reference
World average			1.68	0.079	0.08	0.6		0.62	Gaillardet et al., 2005
Jinzhou Bay, China	2009	0.03	3.06	0.61	0.92	11.87		2.19	Wang et al., 2012
Liaodong Bay, China	2009	0.14	2.86	3.98	0.66	17.76		5.46	Zhang et al., 2017
Laoshan Bay, China	2017-2018	0.015	1.50	0.81	0.12	1.81	1.23	1.16	Wang et al., 2019
Dingzi Bay, China	2010	0.05	2.02	1.07	0.36	23.83	4.10	1.33	Pan et al., 2014
Zhanjiang Bay, China	2014		4.40	0.23	0.12	12.64	2.70		Zhang et al., 2018
Xiangshan Bay, China	2011-2016	0.062	3.4	1.93	0.22	16.8	0.22	2.6	Zhao et al., 2018
Pearl River, China	2012	0.02	4.06	1.57	0.15	8.06		2.09	Zhen et al., 2016)
East Guangdong coastal, China	2007		2.24	1.94	0.11	14.05	1.20	2.48	(Zhang et al., 2015
West Guangdong coastal, China	2007		1.91	1.81	0.09	11.86	1.27	1.86	Zhang et al., 2015
Daya Bay, China	2005		3.2	2.4	0.041	42.2	2.34	2.25	Qiu et al., 2005
Beibu Gulf	2020-2021	0.08	1.06	0.23	0.03	12.12	0.65	0.62	This study
Grade I		0.05	5	1	1	20	50	20	
Grade II		0.2	10	5	5	50	100	30	

ND, not detected; Grades I-II, the National Standard of China for Seawater Quality GB 3097-1997.

TABLE 6 The results of PCA of heavy metals and other physicochemical parameters in the Beibu Gulf.

	Principal component			
	PC1	**PC2**	**PC3**	**PC4**
T	-0.489	-0.215	0.129	0.382
S	0.674	-0.242	**0.466**	0.000
DO	**0.816**	0.190	-0.216	0.094
pH	**0.688**	-0.309	0.330	0.045
TSM	-0.169	0.053	0.304	**-0.726**
Cr	0.083	**0.518**	**0.394**	0.127
Cu	**-0.394**	**0.569**	0.301	0.086
Cd	**-0.301**	**0.627**	-0.099	0.171
Pb	0.275	**0.571**	**0.329**	0.154
Zn	0.207	**0.570**	0.033	-0.046
As	**-0.508**	-0.283	**0.464**	-0.192
Hg	-0.184	-0.414	0.294	**0.535**
Eigenvalue	2.524	2.125	1.148	1.086
% of variance	21.037	17.712	9.569	9.502
Cumulative variance	21.037	38.749	48.318	57.370

The bold values indicate strong loadings.

coastal bays, particularly in the summer (Figures 4, 5). Previous studies have also reported that high concentrations of Cu and Cd occurred in the coastal bays and the estuary areas with low salinity in the Beibu Gulf (Lao et al., 2019a; Lao et al., 2022a). Heavy metals of Cu and Cd mainly serve as anthropogenic sources (i.e., antifouling paints, smelting and refining) (Wang et al., 2019). In the summer, fishing boats were prohibited from carrying out fishery-related activities in the SCS (about four months from 1st May). During the fishing moratorium, most of these fishing boats docked at the coastal wharf, and the fishermen began to repair and maintain the fishing boats during this period. The use of antifouling paints containing heavy metals could aggravate the contamination of those metals in the water. Moreover, the enhancement of the coastal current due to heavy rainfall during summer, the seawater of the Beibu Gulf is mainly input from the coastal current (43%) (Lao et al., 2022c), which could transport those metals from the coastal bays and the estuary areas to the offshore areas. Thus, the concentrations of Cu and Cd generally showed a decreased trend from the coastal bays to the offshore areas during summer (Figures 5F, 4B).

Similar to Cu and Cd, Cr and Zn are also mainly used in antifouling paints (Wang et al., 2019). In addition, Pb is widely used as the anti-corrosive compound for shipping and the antiknock agent in diesel fuel (Wang et al., 2018; Lao et al., 2022a). Thus, the shipping and mariculture activities mainly contributed to PC2. In addition, the distributions of Cr, Zn and Pb were similar to the Cu and Cd in summer (Figures 4B, F, 5B, F , 7B), which could also be influenced by the coastal current during this season. However, the Cu, Cd, Pb, Zn and Cr were found higher concentrations in the offshore areas during the other three seasons, suggesting that different sources and/or influent factors occurred during those periods. During the spring, fall and winter, with the decrease of the runoff in the northern gulf, the increasing intrusion of the other water masses could carry higher metals from other regions into the gulf (Lao et al., 2022c), resulting in the higher concentrations of those metals were all observed in the offshore areas. In the PC3, high positive loadings for salinity, Cr, Pb and As suggested that those metals may transport with water masses from other areas with higher salinity water. In Beibu Gulf, the higher salinity water in the west-Guangdong coastal current and SCS water are also the two dominant water masses that affect the seawater in the Beibu Gulf, and those water masses could transport a large number of materials to the gulf (Lao et al., 2022c). The proportion of SCS water to the seawater of Beibu Gulf is relatively lower in summer (30%) and fall (31%), while it changes to the dominant seawater in the gulf during winter (57%) (Lao et al., 2022c). By contrast, the contribution of the west-Guangdong coastal current is relatively stable during the whole year (24-31%) (Lao et al., 2022c). Thus, the higher concentrations of heavy metals in the offshore areas during winter may be influenced by the intrusion of SCS water and the west-Guangdong coastal current. Previous studies have reported that higher heavy metal contaminations were observed around the southern coast of Hainan Island, which likely originated from pollution discharge by intensive human activities, such as industrial discharges from port and shipping facilities, agriculture wastes, domestic sewage and frequently fishing activities (Yang et al., 2004; Li and Huang, 2012; Wang et al., 2013; Yang et al., 2019). In addition, with the rapid development of urbanization and industrialization, higher heavy metal contaminations have also been found in the Pearl

River Estuary and the coastal waters of western Guangdong Province (Li et al., 2007; Zhang et al., 2010; Zhang et al., 2015; Zhang et al., 2018; Zhang et al., 2022b; Zhou et al., 2022). The higher heavy metal contamination in those regions would enter into the Beibu Gulf with the water masses, resulting in higher concentrations of heavy metals occurring in the offshore areas of the Beibu Gulf. However, in the spring and fall, the contribution of SCS water to the heavy metals loading in the Beibu Gulf should be less due to its lower contribution to the seawater of the gulf during those seasons (Lao et al., 2022c). Thus, the higher concentrations of heavy metals in the offshore area of Beibu Gulf may mainly originate from the input of the west-Guangdong coastal current during the spring and fall.

In addition, Hg in the coastal bays of the northern Beibu Gulf mainly originated from the terrestrial input (Lao et al., 2022a). The highest concentrations of Hg were observed in summer, when the coastal current was strong due to the heavy rainfall during this period, which could erode a large number of land-based pollutants into the gulf (Lao et al., 2020; Lao et al., 2021b; Chen et al., 2022b), resulting in the high concentrations of Hg appearing in the whole water of the gulf (Figure 6B). However, although the coastal current was weaker in fall than that in summer, the current in the fall is still stronger than in other seasons (Lao et al., 2022c), resulting in the higher concentrations of Hg appearing in the coastal areas in the northern Beibu Gulf (Figure 6C). By contrast, with the weakening of the coastal current in winter and spring, the contribution of the west-Guangdong coastal current and the SCS water to the Beibu Gulf increases, and the concentrations of Hg in the offshore area are higher than that in the coastal areas (Figures 6A, D). The high contaminations of Hg were also reported on the coast of western Guangdong Province and Hainan Island (Hu et al., 2013; Li et al., 2013; Wang et al., 2013; Liu et al., 2014; Zhao et al., 2020), and the metal would input into the Beibu Gulf with the transportation of the water mass. This suggests that the transportation of water masses in Beibu Gulf is greatly influenced on the distribution of Hg in the gulf.

Generally, the seasonal changes of the water masses that affect the seawater of Beibu Gulf greatly affect the distributions of heavy metals in the gulf.

Conclusion

Spatial and seasonal variations in the concentrations of the seven heavy metals were found in the seawater of Beibu Gulf. Seasonally variations in the concentrations of heavy metals were observed in the gulf, which are mainly influenced by human activities (i.e., shipping and mariculture activities) and seasonally hydrological conditions. The higher concentrations of heavy metals generally occurred in the coastal bays or areas during the summer, whereas the higher concentrations were observed in the offshore areas during the other three seasons. This is mainly related to the seasonal changes of the water masses that affect the seawater of Beibu Gulf, such as the dominant contribution of coastal current from the northern gulf in summer, and the dominant contribution of west-Guangdong coastal current from the east and SCS water from the south during the other three seasons. This study reveals that the seasonal changes of the water masses in the Beibu Gulf greatly affect the large-scale distributions of heavy metals in the Beibu Gulf, which is different from previous studies that the coastal heavy metals in the gulf are mainly affected by the northern terrigenous input, providing new insight in the impact of water masses on the distribution of metals in the gulf.

Data availability statement

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

Author contributions

ZZ: conceptualization, sampling, sample analysis, and writing. HW: sampling, sample analysis, and draft preparation. YG: data management and editing. LZ, PS, and QZ: conceptualization. All authors contributed to the article and approved the submitted version.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fmars.2022.996202/full#supplemen tary-material

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