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Distribution characteristics and risk assessment of heavy metals in seawater, sediment and shellfish in the inner and outer Daya Bay, Guangdong

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We investigated the distribution, sources, and ecological risks of heavy metals (As, Hg, Zn, Cd, Pb, Cu, and Cr) in seawater, sediments, and shellfish in the inner and outer waters of Daya Bay. 42 seawater quality survey sites, 21 sediment survey sites and 21 biological survey sites were set up in the study area. Our results showed that Daya Bay's seawater is both clean and has a high Cu exceedance factor. The sediment heavy metal potential ecological hazard indices are all less than 40, which indicates a minimal degree of risk. E_{RI} in the bay (mean value of $E_{RI}$is 25.43) and that outside the bay (mean value of 23.56) is lower than 150, so the potential impact on the ecosystem is relatively low. In the Bay, Hg and Zn are primarily from fossil fuel and coal combustion, which enter the ocean *via* dry and wet deposition or surface runoff. Outside the Bay, Cr, Cu, Zn and Pb are derived the combustion waste gases of ships that enter the ocean *via* atmospheric deposition. Concerningly, arsenic and lead level in shellfish organisms appear to be above the standard values.However, because THQ and TTHQ are less than 1, there is no potential risk to human health. The weekly assessed intakes (EWIs) of Hg, AS, Pb, and Cd in shellfish inside and outside Daya Bay were 0.093 (0.058 outside the Bay), 0.594 (0.534), 1.115 (1.489), and 0.201 (0.190), respectively, all of these values were lower than the provisional PTWI for humans established by WHO. This indicates that the probability of carcinogenic risk to the population from heavy metals in shellfish are all below unacceptable levels.

KEYWORDS

heavy metals, source, health risks, distribution characteristics, shellfish

1 Introduction

Heavy metals are toxic, persistent, and non-degradable heavy elements with densities greater than 4.5 g/cm. Because of their tendency to accumulate in sediments and organisms, heavy metals are a major environmental concern. (Jiang et al., 2012; Chen et al., 2016; Zhang et al., 2016). In recent decades, rapid economic and societal development has resulted in the transport of large amounts of heavy metals to estuaries and coastal bays *via* surface runoff, atmospheric deposition, and wastewater discharge (Huang et al., 2014; Li et al., 2018; Feng et al., 2019). However, the majority of heavy metals are eventually deposited in sediments and incorporated into organisms because they are not easily degraded in the ocean and migrate to other environments. According to relevant studies, China's Bohai Bay, and Quanzhou Bayhave heavy metals. Cu (60.81 mg/kg), Pb (66.98 mg/kg) and Zn (186.7 mg/kg) in Quanzhou Bay sediments, and Cu (38.5 mg/kg) and Cr (101 mg/kg) in Bohai Bay all exceeded the level 1 standard (Gao and Chen, 2012; Yu et al., 2016).

Marine shellfish is one of the main types of seafood in the human diet. Filter feeding and open-cycle respiration are physiological traits that make shellfish vulnerable to exposure to large amounts of seawater. (Yuan et al., 2020). Shellfish typically inhabit the environment near the bottom of the sea, where they live chiefly on zooplankton, such as polychaetes, in the sediment, which allows them to absorb more heavy metals (Hedberg et al., 2014). therefore, the accumulation of heavy metals in edible marine shellfish can directly impact on human health (Saher and Kanwal, 2019; Salam et al., 2019). The tolerance and accumulation of contaminants in shellfish has led to their frequently use as indicators for monitoring marine pollution (Ramu et al., 2007; Farrington et al., 2016).

Daya Bay, located in southeastern Guangdong, is a semi-enclosed bay in an industrial area with abundant marine resources. In recent years, petrochemical parks, nuclear power plants, oil storage and transportation bases, and ports have been actively constructed in Daya Bay (Yu et al., 2016), causing a significant amount of pollutants containing heavy metals to be released into the sea. (Gu et al., 2016). With the second phase of the oil refining project of the China National Offshore Oil Corporation (CNOOC) Huizhou Petrochemical Company Limited and the second phase of the ethylene project of CNOOC Shell Petrochemical Company Limited officially being put into operation in 2017, Daya Bay Petrochemical Industrial Zone has formed an annual production capacity of 22 million tons of oil refining and 2.2 million tons of ethylene. The sewage in Daya Bay Petrochemical Area is discharged by deep sea pipelines for a long time, and the sewage discharge capacity of the first sewage pipeline is 1150 m^3/h (Xu et al., 2014). In July 2017, the second sewage discharge pipeline in Daya Bay Petrochemical Zone was put into use. The sewage discharge pipe orifice was set outside the Daya Bay mouth, and the designed sewage discharge capacity reached 3800 m^3/h (Yang et al., 2019). the pressure on the ecological and environmental quality of the water inside and outside Daya Bay has increased. Less research is currently being done on the outer sea, with most recent domestic and international studies concentrated on the area inside Daya Bay. In addition, few studies have looked into the potential risks to human health. In this study, we investigated the spatial distribution characteristics of heavy metals (As, Hg, Zn, Cd, Pb, Cu, and Cr) in the inner and outer waters of Daya Bay, Guangdong, and identified the pollution level, sources, and human health risks of heavy metals to provide a scientific foundation for the prevention and control of local metal pollution.

2 Material and methods

2.1 Study area

Daya Bay (22° 30′ - 22° 50′ N, 114° 29′ - 114° 49′ E) is located in the eastern part of Guangdong Province between Honghai Bay and Dapeng Bay and is a typical subtropical semi-enclosed shallow bay. There are more than 50 islands in Daya Bay, and a series of north-south oriented islands in the center of the bay (Central Island) divide the bay into two parts: the eastern entrance that is approximately 9.6 km wide and 19-20 km deep; and the western entrance that is approximately 5.4 km wide and 19 m deep (Xu, 1989). The exchange of seawater with external seawater mainly occurs through the mouth of the bay. The movement of seawater is mainly controlled by the tide wave and topography of the South China Sea, and the tidal type is an irregular semi-daily mixed tide.

Since the 1980s, Daya Bay has vigorously developed petrochemical-based industries, the good ecological environment has led to the rapid development of aquaculture, two nuclear power plants located on the west coast were put into operation in 1994 and 2002, and the first and second deep-sea outfall pipelines were put into operation in 2000 and 2017, respectively. These anthropogenic activities have led to heavy metal contamination of seawater, sediments and organisms in Daya Bay.

2.2 Samples collection and analysis

In November 2021, 42 seawater quality survey points, 21 sediment survey points, and 21 biological survey points were investigated in the study area; the specific sampling stations are shown in Figure 1. All samples were collected and preserved according to the Marine Monitoring Code (GB17378.3-2007) (Ma et al., 2008). Seawater samples were collected using water quality samplers, and 500 mL of seawater samples were loaded into the sampling bottles and stored in low-temperature

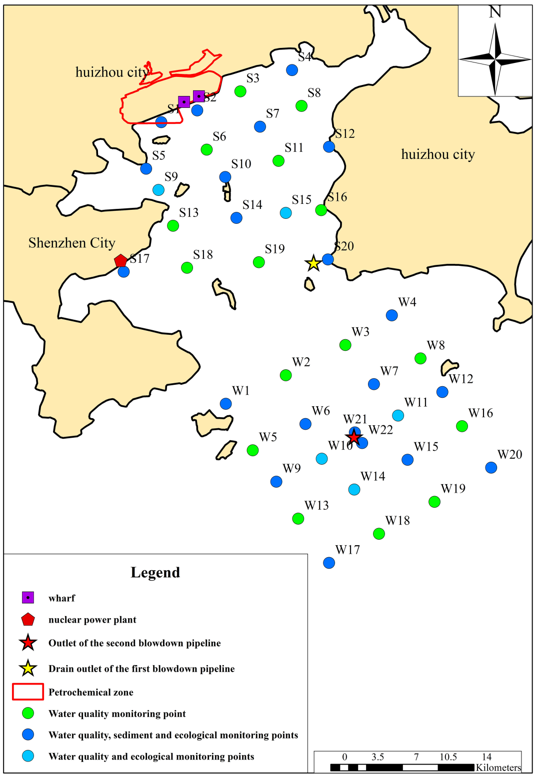

FIGURE 1
Monitoring points in the study area.

refrigerated conditions. When the water depth was less than 10 m, only surface samples were collected; when the water depth was greater than 10 m and less than 25 m, both surface and bottom water samples were collected; when the water depth was greater than 25 m, the surface, middle, and bottom water samples were collected. The depth of surface seawater was in the range of 0-1 m; that of the middle seawater layer was 10 m; and that of the bottom seawater layer was 2 m from the bottom. The pretreated elements Hg and As were determined by atomic fluorescence (BAF-2000), Cr by flameless atomic absorption spectrophotometry (PinAAcle 900T), and Cu, Pb, Zn, and Cd by anodic dissolution voltammetry (797VA).

Sediment samples were collected using a winch connected to a grab mud collector at the surface of the seawater bottom from 0 to 5 cm, packed into polyethylene bags, and stored under refrigeration at 0-4°C. Sediment samples were stored in a dry and ventilated environment, ground in an agate bowl, and then passed through a 160 mesh nylon sieve. After pretreatment, Hg and As were determined by atomic fluorescence method (BAF-2000), and Cu, Pb, Zn, Cd and Cr were analyzed by inductively coupled plasma mass spectrometry (ICP-MS DRCe). Organic carbon is determined by potassium dichromate redox volumetric method.

Fish, crustaceans and shellfish were caught in the trawl, but relevant research shows that shellfish are more seriously polluted by heavy metals. Therefore, this paper mainly studies the biological quality of Perna viridis and Ruddy Clam shellfish. Biological samples were trawled at a speed of 10 knots/h, and samples with a weight of approximately 1.5 kg were selected and rinsed on-site with seawater and subsequently frozen and stored. After dissecting the biological samples, 200 mg of muscle tissue samples were extracted by 24-h freeze-drying using HNO3-H2O2 (4:2) acidification, placed into an electric heating plate, and heated to 120-140°C. After pretreatment, elemental Hg was determined by atomic fluorescence spectrometry (AFS-8520), and As, Cu, Pb, Zn, Cd, Cr were analyzed by inductively coupled plasma mass spectrometry (7800 ICP-MS).

During the measurement of seawater samples, the standard solutions of Cu, Pb, Zn, Cd and Cr (GBW (E) 080040), Hg (GBW08617) and As (GBW (E) 080117) are used as calibration standards. The quality control shall be carried out with reference materials specified in China Offshore Marine Sediment Standard Material (GBW 07314) and China National Standard Material GBW 10024 (GSB-15). The error of parallel samples was less than 5%, and the recoveries of the standard substances were between 95 and 110%.

According to the Marine Monitoring Code (GB 17378-2007), when a few measured values (less than 50% of the total) were below the detection limit, the measured value was equal to 50% of the detection limit.

2.3 Analytical assessment method

2.3.1 Evaluation of heavy metal pollution in seawater

The pollution levels of Cu, Pb, Zn, Cd, Cr, Hg, and As in seawater samples were comprehensively evaluated using the water quality integrated pollution index (WQI) method. The formula is as follows:

$$WQI = \frac{1}{n}\sum_{1}^{n}\frac{C_i}{C_{i0}}$$

where C_i is the measured concentration of the heavy metal i; C_{i0} is the first-class standard of the Seawater Quality Standard (GB3097-1997); n is the total number of samples involved in the analysis; and WQI is the comprehensive pollution index of heavy metals at the station. The specific pollution level classification standards are listed in Table 1 (Xu et al., 2014).

2.3.2 Sediment heavy metal risk assessment

In this study, the potential ecological hazard index (PEEI), developed by Hankanson in Sweden, was applied to evaluate the level of heavy metal contamination in sediments (Hakanson, 1980). Compared to the single-factor pollution index, the above

TABLE 1 Classification standard for the pollution level of heavy metals in seawater.

Pollution level	1	2	3	4	5
WQI	<1	1~2	2~3	3~5	>5
Pollution effects	No effect	Slight impact	Moderate impact	Stronger impact	Severe Impact

index considers the synergistic effects, pollution levels, and toxic effects of different heavy metals (Rezaee Ebrahim Saraee et al., 2011; Liu et al., 2021). The formula is as follows:

$$E_f^i = T_f^i \times C_f^i = T_f^i \times \frac{C^i}{C_n^i}$$

where E_f^i is the potential ecological hazard factor of heavy metals; T_f^i is the toxicity response factor of heavy metals; C_f^i is the pollution factor of metals; C^i is the measured concentration of heavy metals; and C_n^i is the evaluation standard of metals (the national standard for Class I sediment was used in this study).

The combined potential ecological hazard index of heavy metals at a single station was the sum of the potential ecological hazard indices.

$$E_{RI} = \sum_1^n E_r^i$$

The individual heavy metal potential ecological hazard index was divided into five levels, from low to high, and the comprehensive potential ecological hazard index was divided into four levels. The potential ecological hazard index evaluation criteria can be used to evaluate the pollution level of single or multiple pollutants at a certain point (Hakanson, 1980; Yi et al., 2016). The evaluation criteria are listed in Table 2.

2.3.3 Volatility of data

The coefficient of variation can quantitatively reflect the differences in the magnitude of pollutant fluctuations at a spatial scale among the survey stations. Using the coefficient of variation to determine the weight of each evaluation factor indicator can reflect the relative importance of evaluation indicators more objectively and weaken the influence of extreme value indicators on the evaluation results. The mathematical expressions for calculating the coefficient of variation are as follows:

$$CV = SD/\bar{X}$$

where CV is the coefficient of variation, SD is the standard deviation of the survey factors at each station, and $\bar{X}$ is the mean value of the survey factors at each station.

2.3.4 Principal component analysis method

Principal component analysis (PCA) is a statistical method that captures the main contradictions. It can reflect most of the information of the original multivariate data by simplifying the data (i.e., replacing more indicators with fewer integrated indicators that originally have some correlation), and achieve a comparable analysis of the data (Granato et al., 2018).

2.3.5 Heavy metal enrichment analysis

The enrichment effects of heavy metals in sediments and organisms in the Daya Bay sea area were evaluated using the sediment-water partition coefficient (K_d), sediment bioconcentration factor (BSAF), and bioconcentration factor (BAF) (Zhang et al., 2015; Yavar Ashayeri and Keshavarzi, 2019). The specific calculation formula is as follows:

$$K_d = \frac{C_{sed}}{C_{sea}}$$

$$BSAF = \frac{C_{org}}{C_{sed}}$$

$$BAF = \frac{C_{org}}{C_{sea}}$$

where C_{sed}, C_{sea}, and C_{Org} indicate the concentrations of heavy metals in sediment, seawater, and marine organisms, respectively. Higher K_d values indicate a higher probability of heavy metals being preferentially trapped by the sediment and vice versa (Liu et al., 2021). When log (Kd)>2.9, it indicates that heavy metals in seawater are preferentially adsorbed in

TABLE 2 Potential ecological harm index evaluation criteria.

E_f^i	Degree	E_{RI}	Degree
<40	low	<150	low
0~ 80	medium	150~ 300	medium
80~ 160	heavier	300~ 600	heavier
160~ 320	heavy	≥600	serious
≥320	serious		

sediments, otherwise they are easily absorbed by organisms (Jung et al., 2005; Yavar Ashayeri and Keshavarzi, 2019). Both BSAF and BAF are used to describe the ability of marine organisms to accumulate heavy metals from surrounding media. A BAF value< 100 or BSAF< 1 indicates a non-significant cumulative effect between the organism and its surroundings (Hao et al., 2019).

2.3.6 Target hazard quotients

The target hazard quotient (THQ) method was used to evaluate the risk of contaminants to human health (Gu et al., 2018). The formula is as follows:

$$THQ = \frac{EF \times ED \times FIR \times c \times 10^{-3}}{\mathrm{RFD} \times \mathrm{WAB} \times \mathrm{TA}}$$

where EF is the frequency of exposure (365 d/year); ED is the years of exposure (average human life span of 70 years); FIR is the human food intake rate (Food and Agriculture Organization of the United Nations (FAO) statistics, where the intake of crustaceans is 5.42 g/d); c is the level of heavy metals in seafood (mg/kg); RFD is the reference daily dose of pollutants (0.0005, 0.001, 0.004, and 0.0003 mg/(kg/d) for Hg, Cd, Pb, and As, respectively); WAB is the average human body weight (60 kg); and TA is the average exposure time to non-carcinogenic sources ((365 d/year) ×ED) (Storelli, 2008). The TTHQ is the sum of the hazard quotients of various heavy metals in seafood. A hazard quotient value less than 1 implies no health risk to human beings when consuming seafood; in contrast, a hazard quotient value greater than 1 implies a certain potential risk to human beings when consuming seafood.

Evaluating the risk to human health from heavy metal intake not only requires an evaluation of the hazard quotient of seafood but also requires the determination of dietary intake. The World Health Organization (WHO) has established provisional tolerable weekly intake (PTWI) values for heavy metals: 5, 7, 25, and 15 μg/(kg/bw) for Hg, Cd, Pb, and As, respectively (Agusa et al., 2007). The formula for the estimated weekly intake (EWI) of heavy metals is as follows:

$$\mathrm{EWI} = \frac{\mathrm{c} \times \mathrm{FIR} \times 7}{\mathrm{WAB}}$$

3 Results and discussion

3.1 Distribution characteristics and pollution assessment of heavy metals in seawater

The results of the water quality evaluation for the sea area are presented in Table 3 and Figure 2. As Cd is basically not detected, this paper will not analyze Cd in seawater. As presented in Table 3, in 2021, except for Cu, the other six factors meet the standard of first-class water in Daya Bay; the maximum exceedance of Cu is 3.3-fold, which appears on W19 outside the bay. The exceedance rate of Cu in the surface layer of seawater in the bay was 15%, whereas those in the surface layer outside the bay were 18.2 and 16.7% in the middle layer and 19% in the bottom layer. This may be ascribed to the large amount of industrial wastewater discharged after the 2nd outfall line of the petrochemical zone of Daya Bay that was operational after 2017, which led to Cu exceedance at some points outside the bay; related studies also showed that the relatively high content of heavy metals at the mouth of Daya Bay may be due to the discharge at the two outfall lines (Liu et al., 2022).

According to the results of the coefficient of variation calculation, The variation coefficients of As in Daya Bay and Pb outside the bay are small, and the variation of other heavy metals is relatively high. Therefore, the seawater in Daya Bay may have originated from different pollution sources.

The comprehensive pollution index of heavy metals in the seawater of the nearshore area of Daya Bay is shown in Figure 3. Figure 3 shows that the average values of the comprehensive pollution index of As, Hg, Zn, Pb, Cu, and Cr of the seawater inside and outside Daya Bay were less than 1. As presented in Table 1, the seawater of Daya Bay is not polluted and the seawater is relatively clean.

The WQI of surface seawater in the bay ranged from 0.052 to 0.624, with a mean value of 0.173. The WQI of surface seawater outside the bay ranged from 0.052 to 0.71, with a mean value of 0.144., and that in the bottom layer ranged from 0.053 to 0.467, with a mean value of 0.141. The WQI shows that the pollution level of seawater inside Daya Bay was higher than that outside it, and the pollution level of the surface layer was higher than that of the bottom layer. Daya Bay is close to the Daya Bay Chemical Industry Park, and the productivity and life along the coast are more frequent. Effluent from enterprises in the petrochemical zone, except the sewage generated by some enterprises (China Shipping Shell Petrochemical Company Limited, CNOOC Huizhou Petrochemical Company Limited, Qingyuan Wastewater Treatment Plant, etc.), which are discharged through the sea discharge pipeline, and the wastewater generated by other industrial enterprises are mainly indirectly discharged into the sea through the rivers entering the sea, resulting in a large number of land-based pollutant sources to the bay. Additionally, the hydrodynamic diffusion conditions in near-shore waters were weaker and slower than those outside the bay. Therefore, the concentration of heavy metals in the bay was higher than that outside the bay.

According to the water quality monitoring data of near-shore waters released by Guangdong Province from 2015 to 2021 (http://gdee.gd.gov.cn/jhszl/index.html) (see Figure 4), Cu and

Pb in the bay showed a fluctuating upward trend, increasing by 177.23 and 384.31%, respectively, in 2021 compared to 2015. Cd, Hg, and As showed a fluctuating downward trend, decreasing by 76.81, 82.43, and 76.70%, respectively (value of As in 2020 compared to that in 2015). The Zn value initially decreased and then increased, with a 6.15% increase in 2020 compared to 2015. The above data indicate a trend of intensified deterioration of Cu and Pb in Daya Bay, wherein the growth proportion of Pb is larger and should be controlled. Except for Cu and Pb, the remaining heavy metals showed an overall decreasing trend. This indicated that in recent years, owing to the continuous strengthening of ecological environmental protection, the emissions of heavy metals other than Cu and Pb have reduced.

The average concentrations of As, Hg, Zn, Cd, Pb, Cu, and Cr in this sea area were lower than those in other similar sea areas (Xiao et al., 2013; Zhang et al., 2017; Zhao et al., 2018; Lao et al., 2019; Nour, 2019). This revealed that the average levels of heavy metals in the nearshore sea area of Daya Bay are lower than those in other sea areas, indicating a lower environmental risk in Daya Bay.

3.2 Distribution and risk assessment of heavy metals in sediments

The silt content of sediment in Daya Bay ranges from 53.28% to 84.14%, clay (mud) 12.56% to 29.93%, silt outside the bay is 66.44% to 81.98%, and clay (mud) 12.89% to 26.57%. The total content of silt and clay (mud) at the survey stations inside and outside the bay is basically more than 90%. The

TABLE 3 Evaluation results of heavy metal quality indices in the sea area.

Carrier	**Regional Location**		**Index**	**concentration: *mg/L***						
				As	**Hg**	**Zn**	**Cd**	**Pb**	**Cu**	**Cr**
seawater	In the Bay	Surface layer	Range	0.5~0.8	0.0007~0.0073	1.3~4.2	0.068	0.163~0.559	0.3~4.3	0.0045~0.1799
			Average	0.6	0.0044	2.4	0.068	0.269	1.1	0.0604
			Standard deviation	0.14	0.55	0.35	/	0.42	0.97	1.01
	Outside the Bay	Surface layer	Range	0.5~0.8	0.00033~0.00349	1.8~12.4	0.061~0.069	0.127~0.191	0.3~4.8	0.0575~0.2362
			Average	0.6	0.00205	6.1	0.065	0.166	0.9	0.1360
			Standard deviation	0.14	0.56	0.54	0.09	0.21	1.31	0.48
		Bottom	Range	0.5~0.9	0.0011~0.0166	2~16	/	0.137~0.328	0.3~3	0.0021~0.1623
			Average	0.6	0.0069	5.7	/	0.185	0.7	0.0537
			Standard deviation	0.18	0.80	0.73	/	0.39	1.02	0.79
Class I standard				0.02	0.00005	0.05	0.005	0.02	0.001	0.001
Carrier	**Regional Location**		**Index**	concentration: *mg/kg*						
				As	**Hg**	**Zn**	**Cd**	**Pb**	**Cu**	**Cr**
Sediment	In the Bay		Range	3.63~9.36	0.022~0.062	61.6~147	0.03~0.14	26.1~50.2	7.6~67.2	38.1~75.6
			Average	6.84	0.04	105.33	0.09	37.07	21.73	58.86
			Standard deviation	0.27	0.26	0.23	0.37	0.22	0.77	0.18
	Outside the Bay		Range	6.4~9.45	0.031~0.05	77~140	0.04~0.1	30~58	11~21.8	43.2~74.8
			Average	7.80	0.04	104.71	0.06	38.21	15.79	54.92
			Standard deviation	0.14	0.15	0.17	0.32	0.20	0.18	0.16
Class I standard				20	0.2	150	0.5	80	35	60
Carrier	**Regional Location**		**Index**	concentration: *mg/kg*						
				As	**Hg**	**Zn**	**Cd**	**Pb**	**Cu**	**Cr**
Biological	In the Bay		Range	0.68~1.09	0.06~0.22	0.4835~0.735	0.25~0.35	1.3~2.9	0.082~0.18	0.3~0.66
			Average	0.92	0.15	0.66	0.31	1.73	0.12	0.39
			Standard deviation	0.14	0.29	0.11	0.12	0.25	0.21	0.41
	Outside the Bay		Range	0.73~0.93	0.04~0.24	0.3675~0.635	0.2~0.45	1.5~3.6	0.099~0.342	0.3~0.84
			Average	0.84	0.09	0.51	0.30	2.36	0.16	0.50
			Standard deviation	0.09	0.81	0.19	0.28	0.30	0.47	0.49
Class I standard				1	0.05	20	0.2	0.1	10	0.5

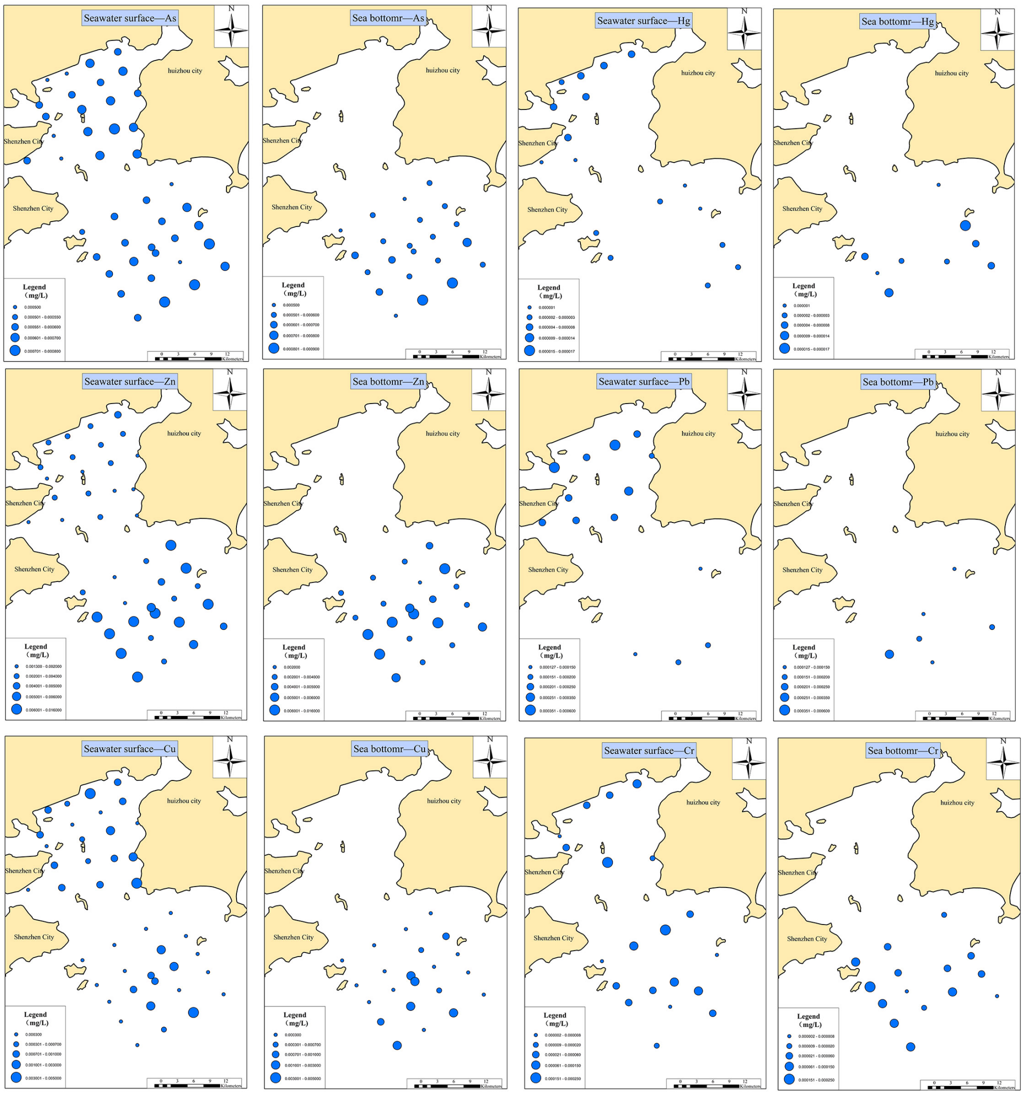

FIGURE 2
Concentration distribution of heavy metals in the seawater of Daya Bay.

average grain size (Mz) of the sediment in the bay ranges from 0.01 to 0.07 mm. Except for S10 (0.07 mm) and S12 (0.03 mm), the average grain size (Mz) of other stations is 0.01 mm. Mz outside the bay ranges from 0.01 to 0.02mm. Except for W6 (0.02mm) and W9 (0.02mm), all other stations are 0.01mm. It shows that the sediments inside and outside Daya Bay are mainly silty sand or clayey silt, mainly silty sand, with a particle size of 0.01 mm.

The heavy metal contents in the sediments of the Daya Bay sea area are presented in Table 3 and Figure 5. As presented in Table 3, The average concentrations of seven heavy metals in and out of the bay are Zn>Cr>Pb>Cu>As>Cd>Hg from high to low. The average concentrations of Cr, Cu, Cd and Zn in the sediments in the bay are higher than those outside the bay. On the contrary, the concentrations of As and Pb are basically the same. Except for the Cu in S1, the heavy metals in the sediments of Daya Bay both inside and outside the sea area do not exceed the Class I standard, and the sediment quality is generally good. S1 station Cu exceeds Class 1 standard. This point is close to the petrochemical base of Daya Bay, and its heavy metal values may be influenced by the industry, resulting in a higher heavy metal content in the sediments. Based on the above phenomena, the heavy metal pollution levels of sediments in Daya Bay were higher than those outside the bay. Related studies have shown that the heavy metals in sediments in the near-shore waters of Daya Bay, such as Yaling Bay, offshore petrochemical areas, and nuclear power plants, are highly distributed but are still at an acceptable level (Qu et al., 2018; Liu et al., 2022).

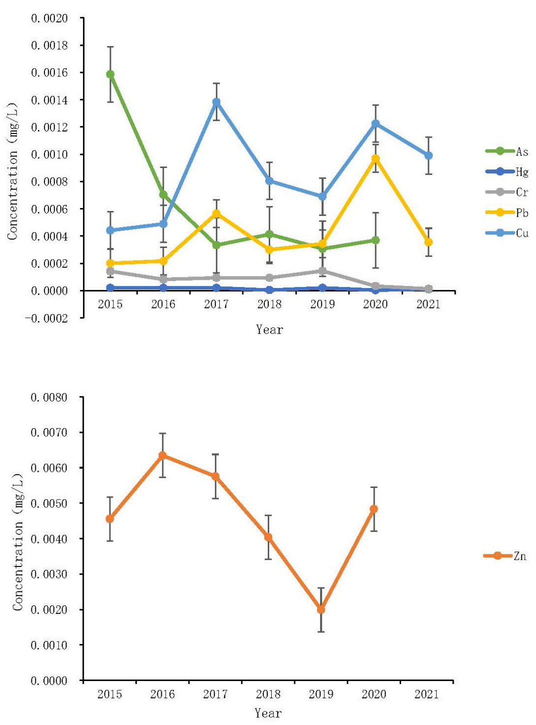

FIGURE 3
WQI of heavy metals in seawater.

The concentration of Cr and Zn in Daya Bay was the highest. As trace metals Cr and Zn are often used as feed additives in mariculture (Siano et al., 2017), resulting in high Cr and Zn contents in the sediment. Therefore, the sediment in Daya Bay was affected by mariculture, resulting in higher concentrations of Cr and Zn than other heavy metals.

The coefficients of variation of Cu and Cd in Daya Bay were 77 and 37%, respectively, which corresponded to high variability (CV > 36%), whereas those of seven heavy metals outside the bay were less than 36%, wherein the highest value was exhibited by Cr (32%). Thus, because Daya Bay is close to petrochemical parks and coastal living areas, each monitoring point is affected by different sewage discharges, resulting in the high dispersion of heavy metals in the sediment. Therefore, we inferred that Cu and Cd in the sediments of Daya Bay may have been influenced by anthropogenic sources, resulting in a high coefficient of variation. Related studies also suggest that high concentrations of Ni, Cu, and Cd in the sediments in the nearshore waters of Daya Bay are caused by human activities (Qu et al., 2018).

The potential ecological hazard index was used to evaluate the heavy metal content in sediments in the study area, and the results showed that (Table 4) the potential ecological hazard index of seven heavy metals inside and outside Daya Bay was less than 40, which was a low hazard level. The average ecological hazard index in the bay was: Hg>Cd>As>Cu>Pb>Cr>Zn, and that outside the bay was: Hg>As>Cd>Pb>Cu>Cr>Zn; notably, the hazard levels of Hg, Cd, and As inside and outside the bay were relatively high. The ecological hazard index method mainly determines the occupancy rate of metals and the toxicity response coefficient of heavy metals. The occupancy rates of Hg and Cd were approximately 0.2, and that of As was below 0.4, which was lower than those of Cu (0.7), Zn (0.7), Pb (0.6), and other heavy metals. The higher hazard levels of Cd, As, and Hg were mainly due to the heavy metal toxicity response coefficients; the toxicity response coefficients of Hg (40), Cd (30), and As (10) were considerably higher than those of Zn (1) and Cu (5), thereby resulting in relatively high hazard levels of Hg, Cd, and As.

The E_{RI} ranged from 12.64 to 42.13 (mean of 25.43) in Daya Bay and 17.49 to 26.62 (mean of 23.56) outside the bay. Except S1 (E_{RI} 42.13) is greater than 40, while other survey stations are lower than 40, indicating that the potential impact of heavy metals in sediments on the ecosystem was relatively low. From each site, S1, S4, S5 and S2 are higher than other sites. From the perspective of spatial distribution, the four survey stations are located near the petrochemical area. This shows that the production activities in Daya Bay Petrochemical Area will increase the potential ecological risks of sediments in the bay. Relevant research also shows that the highest potential ecological risk index of Daya Bay sediment is close to the petrochemical base, which is mainly affected by land sources, and the risk mainly comes from Cd and As (Liu et al., 2018). Therefore, Daya Bay is mainly affected by the petrochemical base, and attention should be paid to the impact of Hg, Cd and As.

Notably, the results produced by the ecological hazard index method varied depending on the background values of the corresponding heavy metals. If the background values of heavy metals of sediments in the Daya Bay sea area calculated by Zhang (Zhang, 1991) and others are used for analysis and evaluation, Hg, Cd, and As values inside and outside the bay are at moderate or heavy ecological hazard levels. In this study, considering the current ecological and environmental management policies in China, and to better support local governments in implementing regional marine environmental management, the analysis and evaluation were conducted with reference to the primary standard of marine sediment quality (GB18668-2002).

The survey data of heavy metals in sediments for the past 10 years indicate that the heavy metal in the Daya Bay sediment shows an initial upward trend and a subsequent downward trend (Zhao et al., 2016; Liu et al., 2018; Tang et al., 2018; Liu et al., 2022). With economic and social development, the petrochemical production capacities of oil refining and ethylene in the Daya Bay petrochemical base are 22 and 2.2 million tons/year, respectively. Moreover, the scale of refining and chemical integration has ranked first in China; thus, the pollutant emissions have increased daily. However, the pollution prevention and control in recent years have

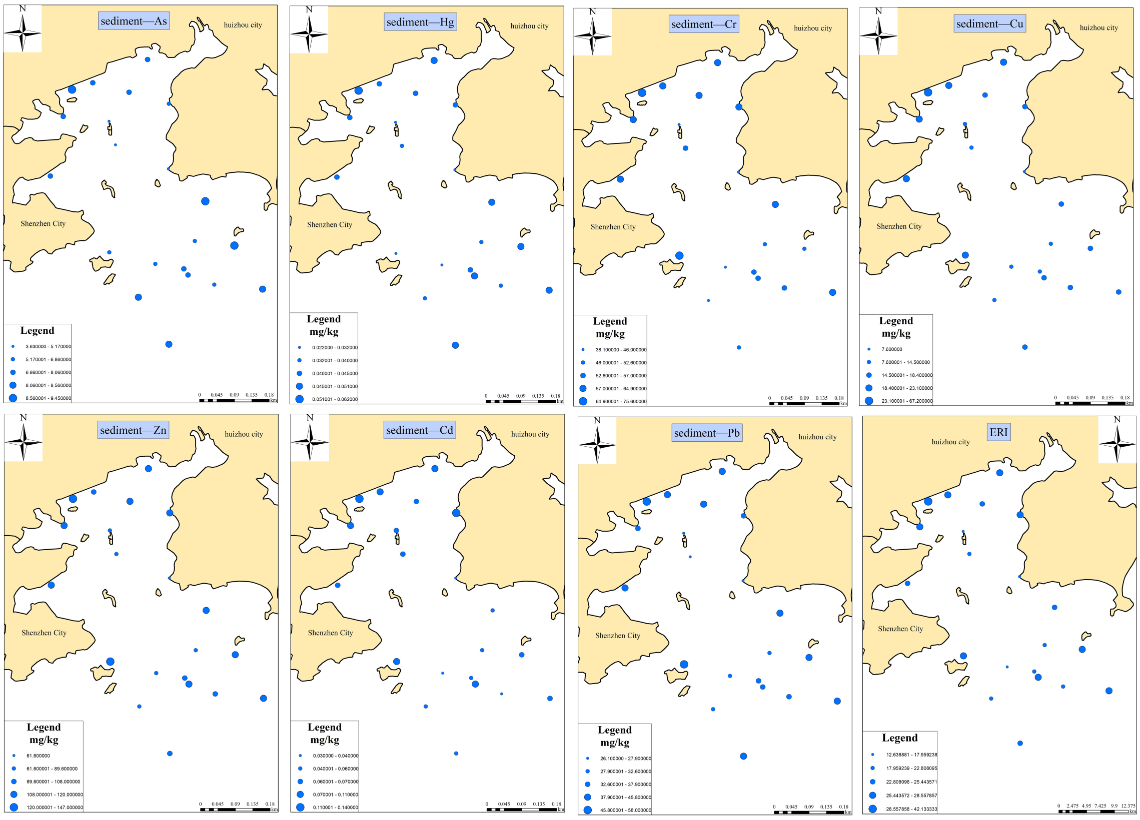

FIGURE 4
Change trend of heavy metals in seawater from 2015 to 2021.

improved the ecological protection requirements and reduced the pollutant emissions. Therefore, the trend of heavy metals in the Daya Bay sediments show an initial increase and subsequent decrease.

Compared to those of other offshore waters, the contents of most heavy metals in the sediments of Daya Bay are at an intermediate level, wherein the contents of Pb and Cr are higher than those in other waters (Zhang et al., 2007; Meng et al., 2008; Gao and Chen, 2012; Fu et al., 2013; Yu et al., 2016; Fan et al., 2022). This further indicates that the pollution of Pb and Cr in Daya Bay is more severe.

3.3 Heavy metal pollution of marine organisms

Two kinds of shellfish were obtained in autumn. The concentrations of As, Hg, Zn, Cd, Pb, Cu and Cr in shellfish are shown in Table 3. The quality standards for shellfish in marine organisms are based on the marine biological quality (GB18421-2001).

The average concentrations of heavy metals inside and outside Daya Bay were 0.92 and 0.84 mg/kg (As), 0.15 and 0.09 mg/kg (Hg), 0.66 and 0.51 mg/kg (Zn), 0.31 and 0.30 mg/kg (Cd), 1.73 and 2.36 mg/kg (Pb), 0.12 and 0.16 mg/kg (Cu), 0.39 and 0.50 mg/kg (Cr), respectively.

The Pb in the shellfish inside and outside the bay exceeded the standards stipulated in the "Marine Biological Quality" (GB18421-2001). As exceeded the standard at S2, S4, S14 and S17 points in the bay, with the rate of exceeding the standard being 33%. Other heavy metal standards met the specified biological quality standards. The average concentration of Pb outside the bay was higher than that inside the bay, indicating that the exceedance of Pb in shellfish outside the bay was more serious than that inside the bay.

As presented in Table 5 and Figure 6, the THQ and TTHQ of the seven heavy metals inside and outside Daya Bay are less than 1, indicating that there is no potential risk to human health from consuming shellfish from the Daya Bay. The order of THQ of all seven metals inside and outside the bay was As>Cu> Cr >Cd>Pb >Zn>Hg. THQ of As is the largest among the seven heavy metals, 0.28 and 0.25 respectively in and out of the bay, and the other six heavy metals are less than 0.1, indicating that mitigating the discharge of As should mainly be prioritized. This is consistent with Yang Liu's conclusion that As is the highest carcinogen (Liu et al., 2022).

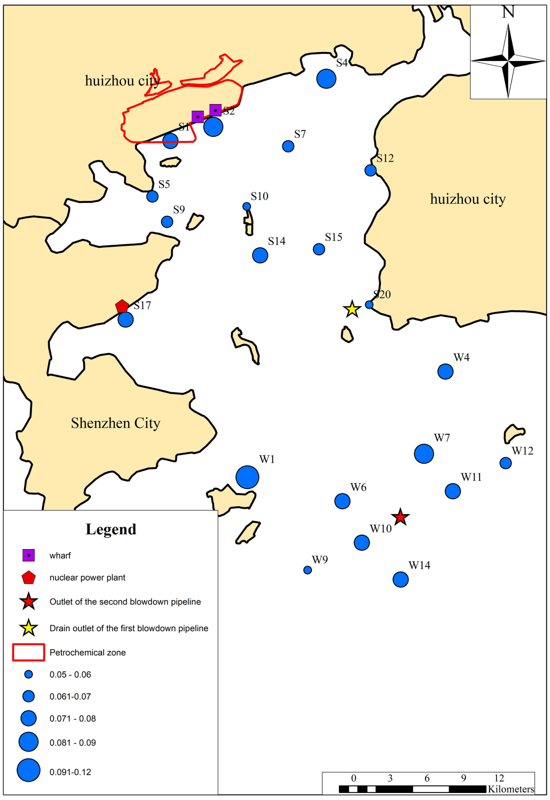

FIGURE 5
Distribution of heavy metals in sediments and potential ecological risks.

The TTHQ in the bay (0.319) was larger than that outside the bay (0.309), indicating that shellfish outside the bay are less hazardous to human health than those inside the bay. Heavy metal pollution in the bay is heavier than that outside the bay due to the influence of coastal chemical parks, such as those in Daya Bay. The BAF inside the bay is higher than that outside the bay, indicating that marine organisms in the bay are more likely to enrich heavy metals from seawater; therefore, heavy metals in marine organisms inside the bay are higher than those outside the bay, resulting in a higher risk inside the bay.

It is particularly noted that metal As is divided into organic forms, which are not toxic, and inorganic forms, which are more toxic. In this paper, the total amount of metal As is measured in the laboratory test analysis. The study proves that arsenic in seafood mainly exists in non-toxic or low-toxic organic form, while the most toxic inorganic arsenic only accounts for 1%-10% of the total arsenic content. Therefore, the carcinogenic risk of As will be lower if 10% of the total arsenic content is used as the inorganic arsenic content for calculation.

The weekly assessed intakes (EWIs) for Hg, As, Pb, and Cd in shellfish inside and outside Daya Bay were calculated to be 0.005 (0.003 outside the Bay), 0.59 (0.53), 0.112 (0.149), and 0.04 (0.038), all of which are lower than the WHO PTWIs for humans. This indicates that the probability of carcinogenic risk to residents for all heavy metals was below unacceptable levels. Overall, the health risks of seafood in Daya Bay were tolerable. With an appropriate reduction in frequency and dose of heavy metals, the carcinogenic risk can be reduced.

3.4 Analysis of the interrelationship and sources of heavy metals

3.4.1 Relevance and sources of heavy metals in seawater

This study showed that the contents of various heavy metals with highly significant correlations have similar spatial distribution patterns to a certain extent. When the significance probability of bilateral test analysis is less than 0.05, it has moderate correlation and homology. Supplement and consummate the concentration of heavy metals in seawater of each station according to the situation near the survey station. Because the detection rate of Cd in the bay and Cd and Pb outside the bay is low. Therefore, correlation analysis is not conducted for them. The results of the Pearson correlation analysis of the heavy metal elements in the seawater of Daya Bay are shown in Figure 7. In addition to the moderate correlation between Hg and Zn in the sea water in the bay, there is no strong correlation between the heavy metals in the sea water in the bay and the outer layer. Therefore, Hg and Zn in the surface seawater inside the bay may have a common source of pollution, and the correlations among the other heavy metals were not significant.

TABLE 4 Potential hazard indices of heavy metals in the sediments.

Regional Location	Index	E_f^i							E_{RI}
		As	Hg	Cr	Cu	Zn	Cd	Pb	
In the Bay	range	1.82~4.68	4.40~12.40	0.95~1.89	1.09~9.60	0.41~0.98	1.80~8.40	2.18~4.18	12.64~42.13
	average	3.42	8.36	1.47	3.10	0.70	5.28	3.09	25.43
Outside the Bay	range	3.20~4.73	6.20~10.00	1.08~1.87	1.57~3.11	0.51~0.93	2.40~6.00	2.50~4.83	17.49~26.62
	average	3.90	8.33	1.37	2.26	0.70	3.82	3.18	23.56

TABLE 5 Marine hazard quotient of Daya Bay.

Region al Location	Index	EWI				THQ							TTHQ
		Hg	AS	Pb	Cd	Hg	AS	Cu	Pb	Zn	Cd	Cr	
In the Bay	range	0.001-0.007	0.046-0.069	0.095-0.183	0.025-0.044	0.0004-0.002	0.022-0.033	0.018-0.033	0.003-0.007	0.002-0.004	0.004-0.006	0.005-0.01	0.254-0.380
	average	0.005	0.594	0.112	0.040	0.001	0.283	0.022	0.004	0.004	0.006	0.006	0.319
Outside the Bay	range	0.001-0.008	0.046-0.059	0.095-0.228	0.025-0.057	0.0004-0.002	0.022-0.028	0.0018-0.006	0.003-0.008	0.0022-0.0038	0.004-0.008	0.005-0.013	0.254-0.359
	average	0.003	0.534	0.149	0.038	0.001	0.254	0.029	0.005	0.003	0.005	0.007	0.306

Principal component analysis (PCA) was used to analyze the heavy metals in the bay and offshore waters. Before principal component analysis, KMO and Baetlet ball tests were conducted. The test results show that KMO inside and outside the bay is less than 0.5. The significance probability of Baetlet sphere test was greater than 0.05. The results show that Daya Bay seawater is not suitable for principal component analysis.

3.4.2 Sediment heavy metal correlations and sources

The results of the Pearson correlation analysis of the heavy metal elements in the sediments of the Daya Bay Sea area are shown in Figure 7. Inside and outside the bay, the particle size of the sediments was negatively correlated with each heavy metal. Inside the bay, particle size was moderately correlated with As and Cr, and particle size had a moderate correlation with Cu and Zn (the probability of significance was less than 0.05) outside the bay. Relevant studies show that there is rich organic matter on the surface of small sized sediments, usually with strong redox potential and stronger enrichment and adsorption capacity. On the contrary, the large particles are rich in silicate, carbonate and other substances, and the redox potential is weak, leading to the greatly weakened surface adsorption capacity. Therefore, heavy metals are not easily adsorbed or enriched (Borg and Jonsson, 1996).

In previous studies, TOC was the main controlling factor affecting the geochemical behavior of sediments and the distribution of heavy metals (Hu et al., 2018). This study shows that organic carbon in the bay has a moderate

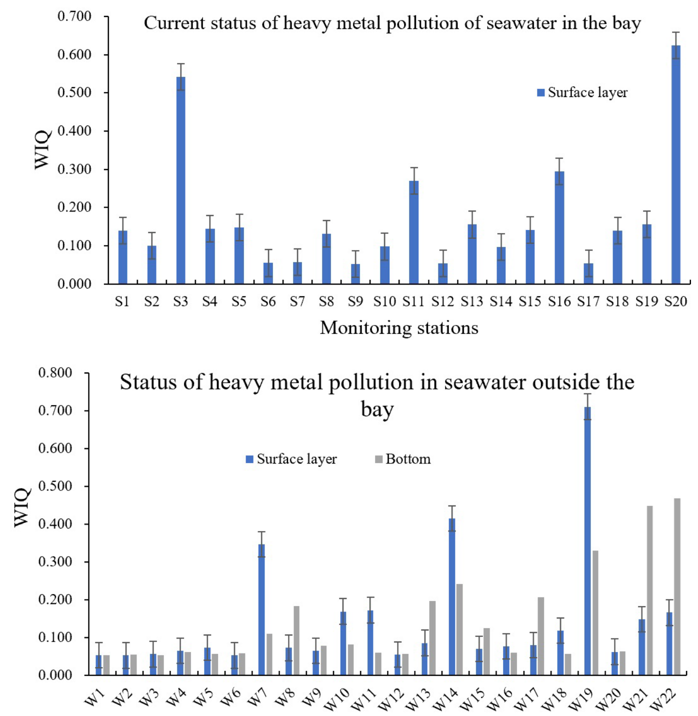

FIGURE 6
Distribution of TTHQ inside and outside Daya Bay.

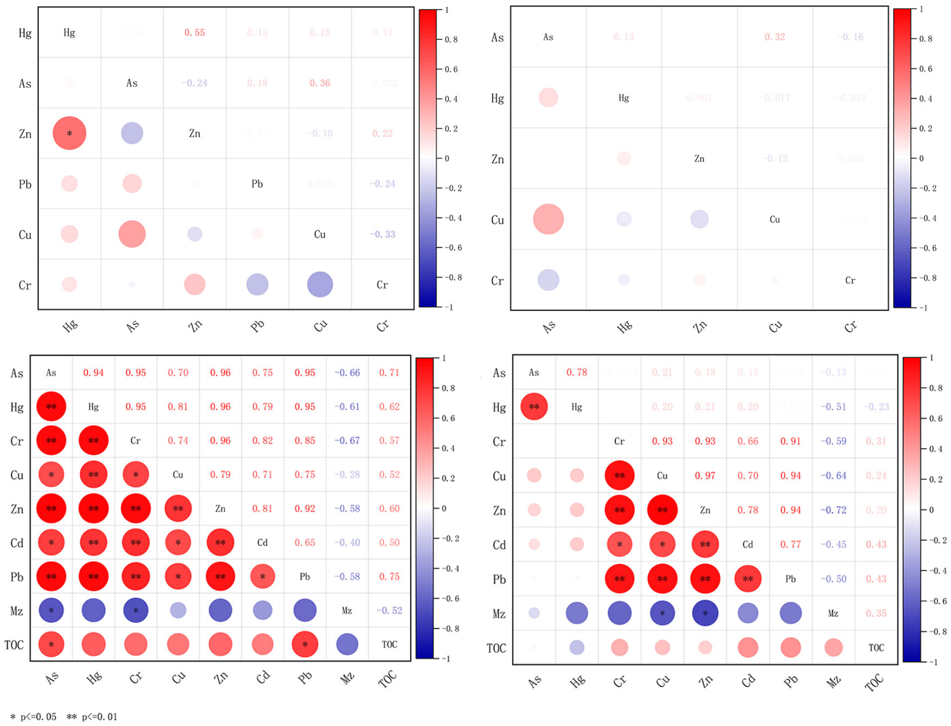

FIGURE 7
Correlation Analysis of Metal Elements in Seawater and Sediment of Daya Bay.

correlation with As and Pb, while other heavy metals have no significant correlation with organic carbon, and organic carbon outside the bay has no significant correlation with heavy metals. This shows that TOC in the bay affects the combination of As, Pb and sediment, but other heavy metals have no obvious correlation with TOC. Organic carbon may be the carrier of As and Pb, but due to the low TOC abundance (<2%), it may not be the main controlling factor for the distribution of metals in sediments. This is similar to the research results of Yao (Yao et al., 2021).

In the bay, the heavy metals showed a moderate positive correlation with each element. It indicates that the heavy metals in the sediments in the bay have the same source. outside the bay, As and Hg had moderate correlations, and Cr, Cu, Zn, and Pb had moderate correlations. It shows that As and Hg in the sediments outside the bay have the same source, and Cr, Cu, Zn, Cd and Pb have the same source.

Principal component analysis (PCA) was conducted for heavy metals in sediments inside and outside the bay. The results are shown in Table 6. Before principal component analysis, KMO and Baetlet ball tests were conducted. The test results show that the KMOs inside and outside the bay are 0.618 and 0.754 respectively, and the KMOs are greater than 0.5. The significance probability of Baetlet's sphere test was 0.00. The results show that principal component analysis can be used to process the data.

The cumulative contribution rate of PC1 principal component in the bay sediments is 86.86% (more than 80%). Hg and Zn (load ≥ 0.4) have higher load in PC1. Indicates that they may have the same source. Zinc is mainly related to fossil fuel combustion (Jones et al., 2014). Mercury containing waste gas generated by fossil fuel and coal combustion enters the environment. The mercury containing catalyst used for petroleum cracking will also be discharged in the form of industrial "three wastes" (Beckers and Rinklebe, 2017). All these will enter the ocean through dry and wet deposition or surface runoff. Therefore, heavy metals in sediment PC1 in the bay mainly come from fossil fuels and coal combustion, and enter the sea through dry and wet sedimentation or surface runoff.

The cumulative contribution rate of the first two principal components of the sediment outside the bay is 89.30%. Cr, Cu, Zn and Pb have higher load in PC1, indicating that they may have the same source. Heavy oil and diesel fuel burned by ships will emit waste gas containing Cu, Pb and Zn (Cheng and Hu, 2010), which will settle into the ocean through the atmosphere. Therefore, this paper speculates that the combustion gas from ships is the main source of PC1 heavy metals.

As and Hg have higher load in PC2, indicating that As and Hg may have the same source. Coal combustion and metal smelting are the two main sources of mercury. As is usually

TABLE 6 Principal component analysis results of heavy metals in Daya Bay sediments.

Regional Location	Principal component	Initial eigenvalue			heavy metals	Load of each item		
		Eigenvalue	Percentage of Variance (%)	Cumulative (%)		PC1	PC2	PC3
In the Bay	PC1	6.08	86.86	86.86	As	0.39	-0.34	-0.16
	PC2	0.42	6.06	92.92	Hg	0.40	-0.11	0.05
	PC3	0.33	4.72	97.64	Cr	0.39	-0.06	-0.25
	PC4	0.09	1.35	99.00	Cu	0.34	0.52	0.74
	PC5	0.04	0.60	99.60	Zn	0.40	-0.09	-0.07
	PC6	0.03	0.38	99.98	Cd	0.34	0.64	-0.54
	PC7	0.00	0.02	100.00	Pb	0.38	-0.42	0.26
Outside the Bay	PC1	4.47	63.89	63.89	As	0.09	0.69	-0.22
	PC2	1.78	25.41	89.30	Hg	0.10	0.69	0.12
	PC3	0.41	5.82	95.12	Cr	0.44	-0.16	-0.31
	PC4	0.23	3.22	98.34	Cu	0.46	0.01	-0.28
	PC5	0.07	1.02	99.36	Zn	0.47	0.00	-0.09
	PC6	0.02	0.34	99.70	Cd	0.39	0.01	0.87
	PC7	0.02	0.30	100.00	Pb	0.45	-0.15	-0.05

associated with petrochemical oil producing areas (Lao et al., 2019). Therefore, PC2 heavy metals mainly come from fuel combustion and industrial production activities in the petrochemical industry.

3.4.3 Heavy metal migration and transformation law

The enrichment results for heavy metals in Daya Bay are presented in Table 7. Kd is used to assess the distribution of heavy metals in seawater and sediments. When log (Kd) is greater than 2.9, it indicates that heavy metals have high affinity with sediments. The average value of log (Kd) in the bay is Cr (6.12) >Pb (5.11) >Zn (4.6) >Cu (4.5) >Hg (4.16) >As (4.04) >Cd (3.01), and that outside the bay is Cr (6.27) >Cu (4.55) >Zn (4.31) >Hg (4.32) >As (4.12). The log (Kd) inside and outside the bay is larger than 2.9, indicating that heavy metals are preferentially adsorbed in the sediment.

The average values of BASF inside and outside the bay are in the order of Cd (0.834 inside the bay, 1.043 outside the bay) > Hg (0.197, 0.120) > As (0.145, 0.113)> Zn (0.131, 0.112) >Cu (0.072, 0.110) >Pb (0.005, 0.007) >Cr (0.003, 0.004). Except that the mean value of Cd outside the bay is greater than 1, the mean value of other heavy metals inside and outside the bay is less than 1.The BASF values of Cd were greater than 1 in S19 and W6, and the heavy metal BASF of each factor in other survey stations was less than 1, indicating that Cd in the sediment was more easily enriched in organisms. Alternatively, Cr, Pb, Zn, Cu, As, and Hg in the sediment environment were not easily enriched in organisms. Lin et al. showed that the metabolism time of Cd in the organism was longer than that of other heavy metals, resulting in a higher concentration of Cd in the organism than that of other heavy metals (Lin et al., 2017). On the other hand, Cd in the sediments of offshore waters is mainly acid soluble (Gao and Chen, 2012; Gao and Li, 2012). The acid soluble metal is the weakest bonding metal in the sediment, which can balance with water, thus becoming more mobile and easy to be used by biology (Castillo et al., 2013; Hu et al., 2013). Therefore, the higher the acid solubility of heavy metals, the easier they flow, and the easier they are to be used biologically, the higher the potential ecological risk to the marine environment. Therefore, Cd in Daya Bay sediments is more likely to be bioaccumulated, so attention should be paid to reducing the input of Cd and reducing the ecological risk of Daya Bay sediments.

The BAF of Cd, Cr, Pb, Zn, Cu, As and Hg are all greater than 100, indicating that the organisms in this sea area have the ability to enrich these seven heavy metals. Because of the filtration and respiration characteristics of bivalves, they are easy to accumulate heavy metals from seawater. The BAF of Cr, Cu and Zn is the highest. It shows that shellfish marine organisms are easy to enrich Cr, Zn and Cu in seawater. Because Cu and Zn are trace metals necessary for shellfish life activities. Therefore, shellfish has a stronger ability to enrich Zn and Cu than other heavy metals. However, Cr is not an essential trace element, which further indicates that the shellfish in this sea area has a stronger ability to enrich Cr. The average value of BAF in bivalves ranges from 286 to 89362, indicating that shellfish are very sensitive to the pollutant level of heavy metals in seawater and are vulnerable to the concentration of heavy metals in seawater. Therefore, controlling heavy metals in seawater can reduce the concentration of marine organisms and reduce potential ecological risks.

4 Conclusion

This study uses various methods to assess the distribution characteristics and ecological risks of heavy metals in seawater,

TABLE 7 Heavy metal enrichment capacity of marine organisms in Daya Bay.

Type	area	Monitoring point	As	Hg	Zn	Cd	Pb	Cu	Cr
Kd	In the Bay	S1	4.27	4.28	4.79	/	/	4.87	/
		S2	4.19	3.78	4.48	/	/	4.53	6.01
		S4	4.12	3.94	4.43	/	/	4.36	5.80
		S5	4.11	3.97	4.47	/	4.83	4.41	7.16
		S7	4.13	/	4.65	/	5.07	4.79	/
		S10	3.80	/	4.67	3.01	/	4.33	/
		S12	4.06	/	4.75	/	5.33	4.73	/
		S14	3.87	/	4.58	/	/	4.30	5.49
		S17	4.10	4.84	4.82	/	5.24	4.80	/
		S19	3.71	/	4.37	/	5.09	3.88	/
	Outside the Bay	W1	4.08	4.18	4.78	/	/	4.86	7.20
		W4	4.26	4.63	4.24	/	/	4.77	6.15
		W6	4.03	/	4.63	/	/	4.56	/
		W7	4.03	/	4.27	/	/	3.76	/
		W9	4.15	/	4.12	/	/	4.64	5.90
		W12	4.13	/	4.65	/	/	4.75	6.80
		W15	4.14	/	4.09	/	/	4.72	5.69
		W17	4.15	/	3.96	/	/	4.73	6.53
		W20	4.08	4.16	4.35	/	/	4.77	/
		W21	4.10	/	4.31	/	/	4.21	/
		W22	4.12	/	3.98	/	/	4.24	5.60
BSAF	In the Bay	S1	0.09	0.15	0.08	0.36	0.00	0.03	0.00
		S2	0.14	0.21	0.14	0.64	0.00	0.07	0.01
		S4	0.13	0.18	0.12	0.78	0.01	0.06	0.01
		S5	0.13	0.19	0.12	0.55	0.00	0.05	0.00
		S7	0.12	0.14	0.13	1.00	0.00	0.06	0.00
		S10	0.19	0.24	0.18	0.86	0.01	0.06	0.00
		S12	0.14	0.12	0.11	0.50	0.01	0.08	0.00
		S14	0.20	0.19	0.17	1.00	0.01	0.10	0.00
		S17	0.13	0.16	0.11	1.00	0.00	0.06	0.00
		S19	0.19	0.41	0.16	1.67	0.00	0.16	0.00
	Outside the Bay	W1	0.13	0.38	0.09	0.60	0.00	0.16	0.01
		W4	0.10	0.07	0.11	1.00	0.01	0.10	0.00
		W6	0.14	0.06	0.12	2.00	0.01	0.13	0.00
		W7	0.12	0.08	0.12	0.80	0.01	0.14	0.01
		W9	0.09	0.08	0.13	1.00	0.00	0.08	0.00
		W12	0.09	0.06	0.10	0.86	0.00	0.06	0.00
BAF	In the Bay	S1	1620	2752	4958	/	/	2000	/
		S2	2180	1251	4083	/	/	2367	5651
		S4	1717	1543	3333	/	/	1389	3287
		S5	1617	1747	3462	/	286	1178	33333
		S7	1600	/	5760	/	455	3567	/
		S10	1229	/	8235	882	/	1367	/
		S12	1567	/	6250	/	1104	4200	/
		S14	1457	/	6500	/	/	2000	834
		S17	1683	10703	7556	/	802	3667	/
		S19	971	/	3719	/	613	1230	/
	Outside the Bay	W1	1618	5644	5522	/	/	11400	89362

(Continued)

TABLE 7 Continued

Type	area	Monitoring point	As	Hg	Zn	Cd	Pb	Cu	Cr
		W4	1800	2752	1879	/	/	5767	3448
		W6	1550	/	5028	/	/	4633	/
		W7	1283	/	2208	/	/	830	/
		W9	1217	/	1758	/	/	3400	2609
		W12	1271	/	4560	/	/	3300	17857

sediments, and organisms inside and outside Daya Bay. The research results show that the seawater inside and outside Daya Bay is clean, and the exceedance factor of Cu is high. Cu and Pb in the bay tend to aggravate the deterioration. The potential ecological hazards of Hg, Cd, and As in the sediments inside and outside the bay are relatively high, but the overall degree of hazards is low. Pb in shellfish inside and outside Daya Bay exceeded the standard, and As in shellfish exceeded the standard at some points in the bay. Although there is no potential risk to human health from consuming shellfish in Daya Bay, the health risks of Pb and As to humans still need to be considered. The quality of seawater is especially important for those who eat seafood because heavy metals in seawater are easily enriched in organisms, which are very sensitive to pollutants in seawater. The heavy metals in Daya Bay sediments mainly come from the combustion of fossil fuels and coal, and the waste gas from ship combustion, which enters the sea through dry and wet sedimentation or surface runoff. Heavy metals in seawater are preferentially adsorbed by sediments. Shellfish have strong adsorption of Cr, Zn and Cu. In general, the quality of seawater and sediments in Daya Bay is generally good; however, owing to rapid industrial development, it is essential to continuously improve environmental standards to reduce the discharge of heavy metal pollutants and the risk to human health.

Data availability statement

The datasets presented in this study can be found in online repositories. The names of the repository/repositories and accession number(s) can be found in the article/Supplementary Material.

Ethics statement

The animal study was reviewed and approved by South China Institute of Environment Sciences, Ministry of Environment Protection of PRC.

Author contributions

XY: writing-original draft preparation, investigation, writing-review and editing, and resources. WZ: writing-review and editing, software, and resources. LS: resources. XZ: resources. QC: investigation and experimental analysis. MH: investigation and experimental analysis. GB: providing revision of the figure, check for content, and approval for publications of the content that are added in the citation in the revised manuscript. Relevant data of heavy metals in seawater that need to be supplemented in the manuscript are provided. All authors contributed to the article and approved the submitted version.

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.

Publisher's note

Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fmars.2022.1064287/full#supplementary-material

References

Agusa, T., Kunito, T., Sudaryanto, A., Monirith, I., Kan-Atireklap, S., Iwata, H., et al. (2007). Exposure assessment for trace elements from consumption of marine fish in southeast Asia. *Environ. Pollut.* 145 (3), 766–777. doi: 10.1016/j.envpol.2006.04.034

Beckers, F., and Rinklebe, J. (2017). Cycling of mercury in the environment: Sources, fate, and human health implications: A review. *Crit. Rev. Environ. Sci. Technol.* 47 (9), 693–794. doi: 10.1080/10643389.2017.1326277

Borg, H., and Jonsson, P. (1996). Large-Scale metal distribution in Baltic Sea sediments. *Mar. Pollut. Bull.* 32 (1), 8–21. doi: 10.1016/0025-326X(95)00103-T

Castillo, A. M. L., Trujillo, I. S., Alonso, E. V., de Torres, A. G., and Pavón, J. M. C. (2013). Bioavailability of heavy metals in water and sediments from a typical Mediterranean bay (Málaga bay, region of andalucía, southern Spain). *Mar. Pollut. Bull.* 76 (1-2), 427–434. doi: 10.1016/j.marpolbul.2013.08.031

Chen, C.-F., Ju, Y.-R., Chen, C.-W., and Dong, C.-D. (2016). Vertical profile, contamination assessment, and source apportionment of heavy metals in sediment cores of kaohsiung harbor, Taiwan. *Chemosphere* 165, 67–79. doi: 10.1016/j.chemosphere.2016.09.019

Cheng, H., and Hu, Y. (2010). Lead (Pb) isotopic fingerprinting and its applications in lead Pollution studies in China: A review. *Environ. Pollut.* 158 (5), 1134–1146. doi: 10.1016/j.envpol.2009.12.028

Fan, Y., Chen, X., Chen, Z., Zhou, X., Lu, X., Liu, J., et al. (2022). Pollution characteristics and source analysis of heavy metals in surface sediments of luoyuan bay, fujian. *Environ. Res.* 203, 111911. doi: 10.1016/j.envres.2021.111911

Farrington, J. W., Tripp, B. W., Tanabe, S., Subramanian, A., Sericano, J. L., Wade, T. L., et al. (2016). Edward D. goldberg's proposal of "the mussel watch": Reflections after 40 years. *Mar. Pollut. Bull.* 110 (1), 501–510. doi: 10.1016/j.marpolbul.2016.05.074

Feng, W., Guo, Z., Peng, C., Xiao, X., Shi, L., Zeng, P., et al. (2019). Atmospheric bulk deposition of heavy metal(loid)s in central south China: Fluxes, influencing factors and implication for paddy soils. *J. Hazardous Materials* 371, 634–642. doi: 10.1016/j.jhazmat.2019.02.090

Fu, W., Meng, F., Wang, Z., Wang, Q., Li, Y., Zhou, Y., et al. (2013). Heavy metals in the intertidal sediments and two marine bivalves along the beibu bay: Contamination status and bioaccumulation. *Acta Scientiae Circumstantiae* 33 (5), 1401–1409. doi: 10.13671/j.hjkxxb.2013.05.041

Gao, X., and Chen, C.-T. A. (2012). Heavy metal Pollution status in surface sediments of the coastal bohai bay. *Water Res.* 46 (6), 1901–1911. doi: 10.1016/j.watres.2012.01.007

Gao, X., and Li, P. (2012). Concentration and fractionation of trace metals in surface sediments of intertidal bohai bay, China. *Mar. Pollut. Bull.* 64 (8), 1529–1536. doi: 10.1016/j.marpolbul.2012.04.026

Granato, D., Santos, J. S., Escher, G. B., Ferreira, B. L., and Maggio, R. M. (2018). Use of principal component analysis (PCA) and hierarchical cluster analysis (HCA) for multivariate association between bioactive compounds and functional properties in foods: A critical perspective. *Trends Food Sci. Technol.* 72, 83–90. doi: 10.1016/j.tifs.2017.12.006

Gu, Y.-G., Wang, X.-N., Lin, Q., Du, F.-Y., Ning, J.-J., Wang, L.-G., et al. (2016). Fuzzy comprehensive assessment of heavy metals and Pb isotopic signature in surface sediments from a bay under serious anthropogenic influences: Daya bay, China. *Ecotoxicol. Environ. Saf.* 126, 38–44. doi: 10.1016/j.ecoenv.2015.12.011

Gu, Y.-G., Ning, J.-J., Ke, C.-L., and Huang, H.-H. (2018). Bioaccessibility and human health implications of heavy metals in different trophic level marine organisms: A case study of the south China Sea. *Ecotoxicol. Environ. Saf.* 163, 551–557. doi: 10.1016/j.ecoenv.2018.07.114

Hakanson, L. (1980). An ecological risk index for aquatic Pollution control. A sedimentological approach. *Water Res.* 14 (8), 975–1001. doi: 10.1016/0043-1354(80)90143-8

Hao, Z., Chen, L., Wang, C., Zou, X., Zheng, F., Feng, W., et al. (2019). Heavy metal distribution and bioaccumulation ability in marine organisms from coastal regions of hainan and zhoushan, China. *Chemosphere* 226, 340–350. doi: 10.1016/j.chemosphere.2019.03.132

Hedberg, Y. S., Lidén, C., and Wallinder, I. O. (2014). Correlation between bulk- and surface chemistry of cr-tanned leather and the release of cr (III) and cr (VI). *J. Hazardous Materials* 280, 654–661. doi: 10.1016/j.jhazmat.2014.08.061

Huang, P., Li, T.-G., Li, A.-C., Yu, X.-K., and Hu, N.-J. (2014). Distribution, enrichment and sources of heavy metals in surface sediments of the north yellow Sea. *Continental Shelf Res.* 73, 1–13. doi: 10.1016/j.csr.2013.11.014

Hu, B., Li, G., Li, J., Bi, J., Zhao, J., Bu, R., et al. (2013). Spatial distribution and ecotoxicological risk assessment of heavy metals in surface sediments of the southern bohai bay, China. *Environ. Sci. Pollut. Res.* 20 (6), 4099–4110. doi: 10.1007/s11356-012-1332-z

Hu, C., Yang, X., Dong, J., and Zhang, X. (2018). Heavy metal concentrations and chemical fractions in sediment from swan lagoon, China: Their relation to the physiochemical properties of sediment. *Chemosphere* 209, 848–856. doi: 10.1016/j.chemosphere.2018.06.113

Jiang, X., Wang, W., Wang, S., Zhang, B., and Hu, J. (2012). Initial identification of heavy metals contamination in taihu lake, a eutrophic lake in China. *J. Environ. Sci.* 24 (9), 1539–1548. doi: 10.1016/S1001-0742(11)60986-8

Jones, F., Bankiewicz, D., and Hupa, M. (2014). Occurrence and sources of zinc in fuels. *Fuel* 117, 763–775. doi: 10.1016/j.fuel.2013.10.005

Jung, H.-B., Yun, S.-T., Mayer, B., Kim, S.-O., Park, S.-S., Lee, P.-K., et al. (2005). Transport and sediment–water partitioning of trace metals in acid mine drainage: an example from the abandoned kwangyang au–Ag mine area, south Korea. *Environ. Geology* 48 (4), 437–449. doi: 10.1007/s00254-005-1257-7

Lao, Q., Su, Q., Liu, G., Shen, Y., and Chen Lei, F. X. (2019). Spatial distribution of and historical changes in heavy metals in the surface seawater and sediments of the beibu gulf, China. *Mar. Pollut. Bull.* 146, 427–434. doi: 10.1016/j.marpolbul.2019.06.080

Li, Y., Zhou, S., Zhu, Q., Li, B., Wang, J., Wang, C., et al. (2018). One-century sedimentary record of heavy metal Pollution in western taihu lake, China. *Environ. Pollut.* 240, 709–716. doi: 10.1016/j.envpol.2018.05.006

Lin, L. H., Wei, H. J., and Huang, H. M. (2017). Contamination status and bioaccumulation of the heavy metals in the surface sediments and benthos in daya bay. *Ecol. Sci.* 36, 173–181 doi: 10.14108/j.cnki.1008-8873.2017.06.024

Liu, J.-J., Ni, Z.-X., Diao, Z.-H., Hu, Y.-X., and Xu, X.-R. (2018). Contamination level, chemical fraction and ecological risk of heavy metals in sediments from daya bay, south China Sea. *Mar. Pollut. Bull.* 128, 132–139. doi: 10.1016/j.marpolbul.2018.01.021

Liu, R., Jiang, W., Li, F., Pan, Y., Wang, C., Tian, H., et al. (2021). Occurrence, partition, and risk of seven heavy metals in sediments, seawater, and organisms from the eastern sea area of Shandong peninsula, yellow Sea, China. *J. Environ. Manage.* 279, 111771. doi: 10.1016/j.jenvman.2020.111771

Liu, Y., Kuang, W., Xu, J., Chen, J., Sun, X., Lin, C., et al. (2022). Distribution, source and risk assessment of heavy metals in the seawater, sediments, and organisms of the daya bay, China. *Mar. Pollut. Bull.* 174, 113297. doi: 10.1016/j.marpolbul.2021.113297

Ma, Y. A., Xu, H. Z., Yu, T., He, G. K., Zhao, Y. Y., and Fu, Y. Z. (2008). *The specification for marine monitoring-part 5: Sediment analysis* (Beijing: China Standardization Press).

Meng, W., Qin, Y., Zheng, B., and Zhang, L. (2008). Heavy metal Pollution in tianjin bohai bay, China. *J. Environ. Sci.* 20 (7), 814–819. doi: 10.1016/S1001-0742(08)62131-2

Nour, H. E. S. (2019). Distribution, ecological risk, and source analysis of heavy metals in recent beach sediments of sharm El-sheikh, Egypt. *Environ. Monit. Assess.* 191 (9), 546. doi: 10.1007/s10661-019-7728-1

Qu, B., Song, J., Yuan, H., Li, X., and Li Duan, N. L. (2018). Intensive anthropogenic activities had affected daya bay in south China Sea since the 1980s: Evidence from heavy metal contaminations. *Mar. Pollut. Bull.* 135, 318–331. doi: 10.1016/j.marpolbul.2018.07.011

Ramu, K., Kajiwara, N., Sudaryanto, A., Isobe, T., Takahashi, S., Subramanian, A., et al. (2007). Asian Mussel watch program: contamination status of polybrominated diphenyl ethers and organochlorines in coastal waters of Asian countries. *Environ. Sci. Technol.* 41 (13), 4580–4586. doi: 10.1021/es070380p

Rezaee Ebrahim Saraee, K., Abdi, M. R., Naghavi, K., Saion, E., Shafaei, M. A., Oltani, N., et al. (2011). Distribution of heavy metals in surface sediments from the south China Sea ecosystem, Malaysia. *Environ. Monit. Assess.* 183 (1), 545–554. doi: 10.1007/s10661-011-1939-4

Saher, N. U., and Kanwal, N. (2019). Assessment of some heavy metal accumulation and nutritional quality of shellfish with reference to human health and cancer risk assessment: a seafood safety approach. *Environ. Sci. Pollut. Res.* 26 (5), 5189–5201. doi: 10.1007/s11356-018-3764-6

Salam, M. A., Paul, S. C., Noor, S. N. B. M., Siddiqua, S. A., Aka, T. D., Wahab, R., et al. (2019). Contamination profile of heavy metals in marine fish and shellfish. *Global J. Environ. Sci. Manage.* 5 (2), 225–236. doi: 10.22034/gjesm.2019.02.08

Siano, F., Bilotto, S., Nazzaro, M., Russo, G. L., Di Stasio, M., Volpe, M. G., et al. (2017). Effects of conventional and organic feed on the mineral composition of cultured European sea bass (Dicentrarchus labrax). *Aquaculture Nutr.* 23 (4), 796–804. doi: 10.1111/anu.12446

Storelli, M. M. (2008). 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 (8), 2782–2788. doi: 10.1016/j.fct.2008.05.011

Tang, H., Ke, Z., Yan, M., Wang, W., Nie, H., Li, B., et al. (2018). Concentrations, distribution, and ecological risk assessment of heavy metals in daya bay, China. *Water* 10 (6), 780. doi: 10.3390/w10060780

Xiao, R., Bai, J., Huang, L., Zhang, H., Cui, B., Liu, X., et al. (2013). Distribution and Pollution, toxicity and risk assessment of heavy metals in sediments from urban and rural rivers of the pearl river delta in southern China. *Ecotoxicology* 22 (10), 1564–1575. doi: 10.1007/s10646-013-1142-1

Xu, G. (1989). *Environments and resources of daya bay* (Hefei, China: Anhui Science and Technology Publishing House), 10–16.

Xu, S.-N., Li, C.-H., Xu, J.-J., Xiao, Y.-Y., Lin, L., Huang, X.-P., et al. (2014). Pollution by heavy metals in the petrochemical sewage waters of the sea area of daya bay and assessment on potential ecological risks. *Huan Jing ke Xue= Huanjing Kexue* 35 (6), 2075–2084. doi: 10.13227/j.hjkx.2014.06.006

Yang, W. C., Huang, D. J., Chen, J. X., Chen, X. Y., Liu, W., Wang, Y. S., et al (2019). Research on ecological environment quality in the sea area near the second petrochemical sewage pipeline discharge outlet in daya bay. *J. Mar. Sci.* 37, 85–91.

Yao, W., Hu, C., Yang, X., and Shui, B. (2021). Spatial variations and potential risks of heavy metals in sediments of yueqing bay, China. *Mar. Pollut. Bull.* 173, 112983. doi: 10.1016/j.marpolbul.2021.112983

Yavar Ashayeri, N., and Keshavarzi, B. (2019). Geochemical characteristics, partitioning, quantitative source apportionment, and ecological and health risk of heavy metals in sediments and water: A case study in shadegan wetland, Iran. *Mar. Pollut. Bull.* 149, 110495. doi: 10.1016/j.marpolbul.2019.110495

Yi, Y.-J., Sun, J., Tang, C.-H., and Zhang, S.-H. (2016). Ecological risk assessment of heavy metals in sediment in the upper reach of the Yangtze river. *Environ. Sci. Pollut. Res.* 23 (11), 11002–11013. doi: 10.1007/s11356-016-6296-y

Yuan, Y., Sun, T., Wang, H., Liu, Y., Pan, Y., Xie, Y., et al. (2020). Bioaccumulation and health risk assessment of heavy metals to bivalve species in daya bay (South China sea): Consumption advisory. *Mar. Pollut. Bull.* 150, 110717. doi: 10.1016/j.marpolbul.2019.110717

Yu, R., Zhang, W., Hu, G., Lin, C., and Yang, Q. (2016). Heavy metal Pollution and Pb isotopic tracing in the intertidal surface sediments of quanzhou bay, southeast coast of China. *Mar. Pollut. Bull.* 105 (1), 416–421. doi: 10.1016/j.marpolbul.2016.01.047

Zhang, Y. (1991). A background value study on heavy metal elements in the sediments of daya bay. *Tropic oceanology/Redai Haiyang. Guangzhou* 10 (3), 76–80.

Zhang, L., Ye, X., Feng, H., Jing, Y., Ouyang, T., Yu, X., et al. (2007). Heavy metal contamination in western xiamen bay sediments and its vicinity, China. *Mar. Pollut. Bull.* 54 (7), 974–982. doi: 10.1016/j.marpolbul.2007.02.010

Zhang, L., Shi, Z., Zhang, J., Jiang, Z., Wang, F., Huang, X., et al. (2015). Spatial and seasonal characteristics of dissolved heavy metals in the east and west guangdong coastal waters, south China. *Mar. Pollut. Bull.* 95 (1), 419–426. doi: 10.1016/j.marpolbul.2015.03.035

Zhang, L., Shi, Z., Zhang, J., Jiang, Z., Wang, F., Huang, X., et al. (2016). Toxic heavy metals in sediments, seawater, and molluscs in the eastern and western coastal waters of guangdong province, south China. *Environ. Monit. Assess.* 188 (5), 313. doi: 10.1007/s10661-016-5314-3

Zhang, A., Wang, L., Zhao, S., Yang, X., Zhao, Q., Zhang, X., et al. (2017). Heavy metals in seawater and sediments from the northern liaodong bay of China: Levels, distribution and potential risks. *Regional Stud. Mar. Sci.* 11, 32–42. doi: 10.1016/j.rsma.2017.02.002

Zhao, G., Ye, S., Yuan, H., Ding, X., and Wang, J. (2016). Distribution and contamination of heavy metals in surface sediments of the daya bay and adjacent shelf, China. *Mar. Pollut. Bull.* 112 (1-2), 420–426. doi: 10.1016/j.marpolbul.2016.07.043

Zhao, B., Wang, X., Jin, H., Feng, H., Shen, G., Cao, Y., et al. (2018). Spatiotemporal variation and potential risks of seven heavy metals in seawater, sediment, and seafood in xiangshan bay, China, (2011–2016). *Chemosphere* 212, 1163–1171. doi: 10.1016/j.chemosphere.2018.09.020