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Characteristics of Heavy Metals in Seawater and Sediments from Daya Bay (South China): Environmental Fates, Source Apportionment and Ecological Risks

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Abstract: In this study, the spatiotemporal distributions, potential sources, and ecological risks of Hg, Cr, and As in seawater, and Hg, As, Zn, Cd, Pb, and Cu in sediments from Daya Bay were investigated. The five-year average concentrations of Hg, Cr, and As in seawater were 0.020 μg/L, 0.79 μg/L, and 2.08 μg/L, respectively. The five-year average concentrations of Hg, As, Zn, Cd, Pb, and Cu in surface sediments were 0.04 mg/kg, 7.34 mg/kg, 63.81 mg/kg, 0.23 mg/kg, 25.60 mg/kg, and 11.78 mg/kg, respectively. Annual variations in Hg, Cr, and As in seawater exhibited different trends. HMs in sediments, such as As, Zn, Pb, and Cu, exhibited similar annual variations, whereas Hg and Cd exhibited different annual variations. The spatial distribution of metal species in seawater and sediments showed significant variability, and the concentrations decreased gradually from the coast to the open sea. The comprehensive potential ecological hazard index (*RI*) of HMs in sediments indicated a relatively high risk, especially for Hg and Cd contamination. The geoaccumulation indices (I_{geo}) of As, Zn, Pb, and Cu suggested that these metals did not pollute Daya Bay, whereas those of Cd and Hg indicated mild and moderate pollution. The environmental fates of HMs were discussed based on Pearson correlation analysis, revealing that concentrations of HMs were greatly affected by parameters, such as pH, salinity, dissolved oxygen (DO), and total organic carbon (TOC). Principal component and factor analyses indicated that Hg, Cr, As, and dissolved inorganic nitrogen (DIN) in water originated from similar sources, including domestic sewage and wastewater from fishing ports, runoffs, and outlets. For sediments, it was proposed that Cu, Zn, As, Pb, and TOC exhibited similar sources, including cage culture and waste discharge from outlets. Meanwhile, Hg and Cd originated from other point sources, such as a harbor. The study suggests that sustainable management and economic development be integrated to control pollutant emissions in Daya Bay.

Keywords: source apportionment; integrated pollution evaluation; multivariate statistics; sustainable development

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1. Introduction

Heavy metals (HMs) are major pollutants in marine environments because of their persistence, high toxicity, and bioaccumulation properties [1,2]. Once HMs are introduced into the ocean, they bioaccumulate and biomagnify in food webs, harming the ecosystem and human health [3]. HMs in marine environments often originate from various natural and anthropogenic sources, such as geologic weathering, urban runoff, domestic sewage, and industrial and agricultural activities [4]. As a hotspot for land–sea interactions,

bays are affected by human activity, such as wastewater discharge, land use, and land cover transformations [5]. For instance, in Daya Bay (Huizhou, Guangdong Province, China), marine aquaculture, nuclear power plants, petrochemical industries, and industrial enterprises coexist and contribute to HM pollution in water and sediment [6–8].

Chen et al. and Qu et al. analyzed trends and drivers of deteriorating water quality in Daya Bay [9,10]. Yang et al. reported that HMs in surface sediments exhibited a zonal distribution, with a gradual decrease from nearshore to offshore [11]. Zhao et al. did not find high levels of Cd, Cr, Cu, Hg, or Zn in sediments from Daya Bay [12]. Tang et al. reported that Cu, Zn, As, Ni, and Cr were below the acceptable limits, while Hg, Pb, and Cd exhibited moderate to high levels [13]. Liu et al. reported the main contaminants were Cd and As, with their ecological risks "high" and "moderate" levels in sediments from Daya Bay [14]. Yu et al. reported the HM concentration in sediments; however, the potential ecological risk of HM has not been studied [15]. Yang et al. reported the concentrations and ecological risk of HMs, ignoring the toxicities of heavy metals [16]. Although the studies of HM geochemical characters in the sediment of Daya Bay had been conducted in recent years, most of them focused on the contamination levels and ecological risk assessment of surface sediment. The investigation of HMs in a long period is quite limited. A long-term investigation of the bay may provide a clearer picture of the spatiotemporal distribution of these pollutants. Moreover, only water quality or sediment quality were considered for the evaluation of the environment in previous studies. Marine sediments are usually considered as the ultimate sink for HMs in coastal waters; however, an equilibrium exists between sediments and the overlying water. HMs in sediments partition into the water when the equilibrium shifts [17]. With rapid industrialization and economic development in the Daya Bay coastal area, the ecological risk of HMs in the marine environment is becoming a serious problem. Therefore, a long-term investigation considering concentrations and ecological risk assessment of heavy metals in both sediments and seawater in Daya Bay is necessary and realistically significant.

In this study, we investigated spatiotemporal variations of HMs in seawater and sediments from Daya Bay during 2014–2019. Based on the data acquired by investigation and the implementation of statistical analysis methods (such as principal component analysis (PCA); factor analysis (FA); the indices of Nemerow, comprehensive potential ecological hazard (*RI*), and geochemical accumulation (I_{geo})), potential pollution sources and risks in Daya Bay were proposed. The results are expected to provide a basis for bridging the gap between economic development and the sustainable management of Daya Bay.

2. Materials and Methods

2.1. Description of the Study Area

Daya Bay covers an area of about 600 km^2 and is located north of the South China Sea (Figure 1) (22°30′–22°50′ N and 114°29′–114°49′ E); it is surrounded by Hong Kong in the southwest, Dapeng Cove in the west, and Red Bay in the east. Daya Bay is semi-enclosed and is known as a habitat for many marine organisms. Three sub-basins are the important parts of Daya Bay, i.e., Aotou Harbor and Yaling Cove in the northwest, Dapeng Cove in the southwest, and Fanhe Harbor in the northeast. Daya Bay does not receive a discharge from large rivers but has a relatively small drainage area from the Dan'ao, Nanbianzao, and Baigang Rivers. Daya Bay has a broad and flat sea bottom with shoal accumulation and a gradually increasing water depth from the north (2–4 m) to the south (10–17 m).

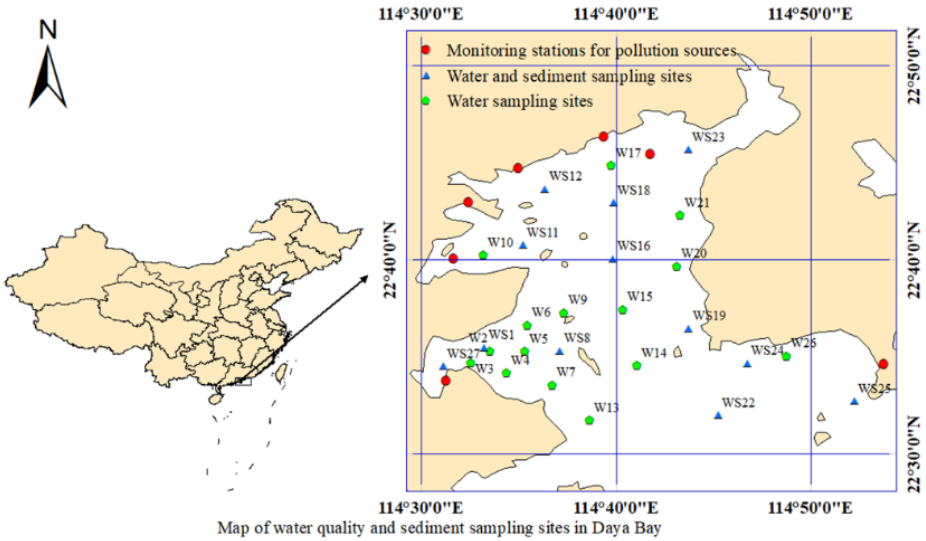

Figure 1. Location of Daya Bay and a sketch map of sampling sites.

2.2. Sample Collection and Analysis

Sampling sites were decided based on various parameters, such as mariculture, nuclear power plant, petrochemical industry, ports, and hydrological conditions around this area in recent years. For the sampling seasons, the investigations were carried out in the flood season. During the flood season, a large amount of industrial wastewater is taken to the sea. Therefore, the investigation during the flood season may be useful for a better understanding of the impact of human activities. Water samples, including surface water and bottom water, were collected from 0.5 m below the surface and 2.0 m above the bottom using 5 L Go-Flo water samplers at 27 sampling sites in the flood season (August) of 2015–2019, and sediment samples (0–5 cm) were collected using a stainless-steel grab sampler at 13 sampling sites in the same season of 2014–2019. The locations of all the sampling sites are shown in Figure 1. Sample collection, storage, and transportation were conducted according to the Specification for Oceanographic Survey (GB/T 12763-2007) [18]. Briefly, water samples obtained with Go-Flo samplers were filtered through acetate membrane filters (0.45 µm pore sizes) and transferred into glass bottles and stored at 4 °C until analysis. Sediment samples were placed into pre-cleaned glass jars and frozen at −20 °C until further treatment. Before analysis, sediments were freeze-dried, ground, and then sieved through a 96 µm stainless steel sieve.

Several important chemical parameters in water (pH, suspended solids (SS), DO, salinity, NH_4^+-N, NO_2^--N, NO_3^--N, Hg, Cr, and As) and sediments (Zn, Pb, Cu, Cd, As, pH, Eh, sulfide, TOC, and Oils) were determined according to the Specification for Marine Monitoring (GB 17378-2007) [19]. Since no continuous data were obtained for Zn, and the detection rates of Pb, Cu, and Cd were low in some years, Zn, Pb, Cu, and Cd in seawater were not included in the study. For HMs in water, only dissolved parts were analyzed. pH values were determined with a pH meter. SS samples were dried and weighed to determine the amount. DO values were determined using the Winkler titration method. The seawater salinity was measured with a salinometer. DIN, including NH_4^+-N, NO_2^--N, and NO_3^--N were analyzed using hypobromite oxidation, zinc cadmium reduction, and N-(1-naphthyl)-ethylenediamine dihydrochloride spectrophotometry methods, respectively. As and Hg in water and sediment samples were tested using atomic fluorescence spectrometry (AFS). Dissolved Cr in water was determined using graphite furnace atomic absorption spectrometry (AAS). Cu, Pb, Zn, and Cd in sediment samples were determined using flame atomic AAS. Sulfide, TOC, and Oils in sediment samples were determined by methylene blue spectrophotometry, potassium dichromate volumetric method, and UV spectrophotometry, respectively. Eh and pH values of sediments were measured with a potentiometer and a pH meter, respectively. Prior to analysis, for dis-

solved Cr, DDTC ($C_5H_{10}NS_2Na$) was used as a chelating reagent, and DDTC-complex in MIBK ($CH_3COCH_2(CH_3)_2$) were extracted for AAS analysis. For dissolved Hg, water samples (100.0 mL) were treated with a mixture of H_2SO_4 (2.0 mL) and $K_2S_2O_8$ (5.0 mL). For As, water samples were treated with thiourea (CH_4N_2S) to reduce the pentavalent arsenic to trivalent arsenic, then potassium borohydride (KBH_4) was added to reduce it to hydrogen arsenide. Sediment samples (0.2000 g) for the measurement of Hg and As were digested with 10.0 mL of a mixture of acid (HNO_3 + HCl). Sediment samples (0.1000 g) for the measurement of Cu, Zn, Cd, and Pb were digested with a mixture of concentrated HNO_3 (1.0 mL) and $HClO_4$ (2.0 mL). Although As is a metalloid that exhibits intermediate properties between those of metals and non-metals, it is referred to as metal throughout this text.

Quality assurance and quality control were evaluated using duplicates, blanks, and standard reference materials (GBW 07333) from the National Research Center for Standard of China. All chemicals used for the analysis were of analytical grade or above. Blanks and duplicates were run for each batch of 10 samples. The blank values were below the detection limits. From the values of the duplicates and reference materials, the relative standard deviation was below 10% for HMs. The recovery of metals in standard reference sediments was normally in the range of 87–113%.

2.3. Pollution and Ecological Risk Assessment Methods

The Nemerow pollution index (P_i) was used to evaluate the sediments as follows [20]:

$$P_{ij} = C_{ij}/S_i \quad (1)$$

$$P_{ijave} = \frac{1}{\mathrm{m}}\sum_{i=1}^{\mathrm{m}} P_{ij} \quad (2)$$

$$P_i = \left\{\left[\left(P_{ijmax}\right)^2 + \left(P_{ijave}\right)^2\right]/2\right\}^{1/2} \quad (3)$$

where P_{ij} is the single factor pollution index of the i^{th} evaluation factor, C_{ij} is the measured concentration of the i^{th} evaluation factor, S_i is the evaluation standard of the ith evaluation factor, m represents the number of evaluation factors, and P_{ijave} and P_{ijmax} refer to the average and maximum single factor pollution indices, respectively. The Nemerow pollution index was divided into five zones to describe pollution levels (Table 1).

Table 1. Pollution zone division for each evaluation index.

Index	I	II	III	IV	V
Single-factor pollution	$P_{ij} \leq 1$ Clean	$1 < P_{ij} \leq 2$ Light	$2 < P_{ij} \leq 3$ Mild	$3 < P_{ij} \leq 5$ Middle level	$P_{ij} > 5$ Serious
Nemerow pollution	$P_i \leq 0.7$ Clean	$0.7 < P_i \leq 1$ Light	$1 < Pi \leq 2$ Mild	$2 < P_i \leq 3$ Middle level	$P_i > 3$ Serious
Geochemical accumulation	$I_{geo} < 0$ Clean	$0 \leq I_{geo} < 1$ Light	$1 \leq I_{geo} < 2$ Mild	$2 \leq I_{geo} < 3$ Middle level	$I_{geo} \geq 3$ Serious
Single index of potential ecological risk	$E^i{}_r \leq 40$ Low	$40 < E^i{}_r \leq 80$ Middle	$80 < E^i{}_r \leq 160$ Relatively high	$160 < E^i{}_r \leq 320$ High	$E^i{}_r > 320$ Extremely high
Comprehensive potential ecological risk	$RI < 150$ Low	$150 \leq RI < 300$ Middle	$300 \leq RI < 600$ Relatively high	$RI > 600$ High	

The pollution status of HMs in sediments was evaluated using the geochemical accumulation index (I_{geo}) as follows [21]:

$$I_{geo} = log_2 \frac{C_i}{1.5 \times C_{Bi}} \quad (4)$$

where C_i is the measured concentration of element i in sediment and C_{Bi} refers to the geochemical background value of an element. The geochemical accumulation index was divided into five zones to describe the pollution levels (Table 1).

The ecological risk was evaluated using the potential ecological risk index (RI) as follows [22]:

$$E_r^i = T_r^i \times C_f^i = T_r^i \times \frac{Ci}{C_{Bi}} \quad (5)$$

$$RI = \sum_{i=1}^{n} E_r^i \quad (6)$$

where E_r^i is the single index of the ecological risk factor, C_f^i is the accumulation factor of metal i, C_i is the concentration of metal i in the sample, C_{Bi} is the geochemical background value of metal i in the sediments, and T_r^i is the toxicity coefficient of metal i. RI was divided into four zones to describe the pollution levels (Table 1).

SPSS 25 was employed to carry out factor analysis (FA) and principal component analysis (PCA) to identify the sources of water and sediment pollution [23–25].

3. Results and Discussion

3.1. Characteristics of HMs in Seawater and Sediments

3.1.1. Seawater

The average concentrations of Hg, Cr, and As in surface water samples over five years were 0.020, 0.78, and 2.03 μg/L, respectively. The average concentrations of Hg, Cr, and As in bottom water samples over five years were 0.020, 0.79, and 2.13 μg/L, respectively. Only a slight difference in HM concentration was found between the surface and bottom water samples. The level of HM concentrations in seawater is considered class I, based on the Sea Water Quality Standard (SWQS) of China (GB 3097-1997) [26].

The temporal variation of HM concentrations (averages of all samples each year) in seawater from Daya Bay is illustrated in Figure 2. The concentrations of Hg (0.022 μg/L), Cr (1.55 μg/L), and As (3.42μg/L) were highest in 2016, 2016, and 2019, respectively. During the five-year continuous monitoring, Hg concentrations did not change significantly. Cr initially increased and then decreased, while As showed the opposite trend. In general, the annual variations for the three metals in seawater exhibited different trends. The reason for this trend may be due to the discharge by industrial enterprises around Daya Bay. In contrast to the inland rivers and reservoirs, the water exchange pattern of Daya Bay was complex as it exerted a significant impact on the dispersion and transport of pollutants, thereby affecting their distributions [27].

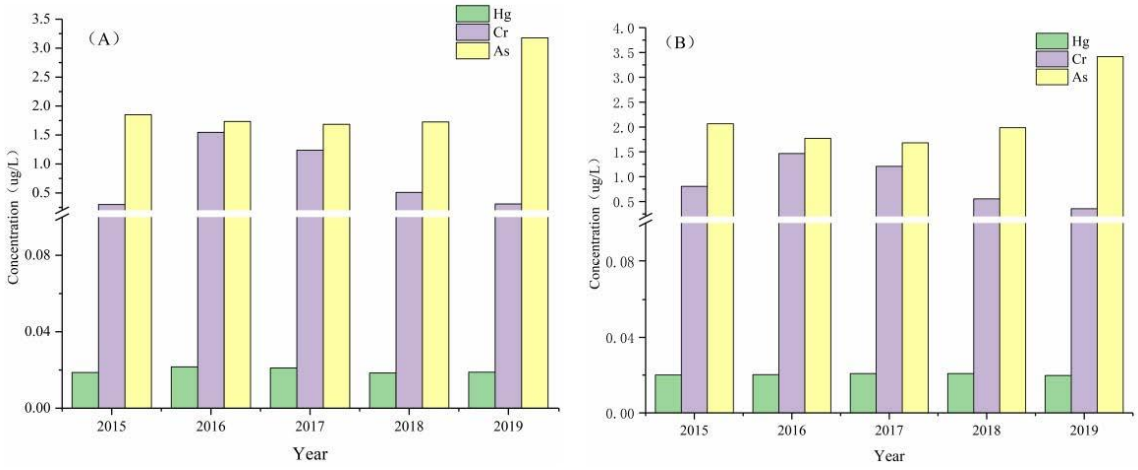

Figure 2. Average concentrations of HMs (μg/L) in surface (**A**) and bottom seawater (**B**) between 2015 and 2019.

Hg concentrations were similar among the sampling sites (Figure 3). High As and Cr concentrations were mainly found in coastal areas (W3, W4, W7, WS8, W10, WS23, WS25, and WS27), which may be related to more frequent human activities near the coast. Water pollutants from domestic, industrial, and aquaculture discharges are the primary sources of HMs near the coast. The far coast is less affected by human activities. Daya Bay has a strong water exchange capacity, which can effectively dilute pollutant concentrations. Therefore, HM concentrations were significantly lower on the far coast [28].

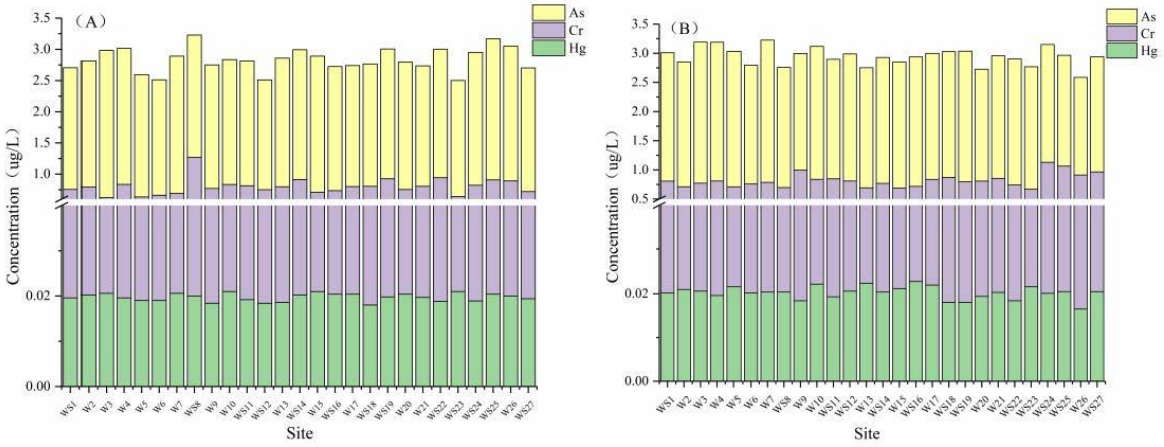

Figure 3. Mean concentrations of HMs (μg/L) in (**A**) surface and (**B**) bottom seawater of each sampling site.

3.1.2. Sediments

Average concentrations each year and average concentrations over five years are presented in Table 2. The level of HM concentrations in sediments is considered as class I, based on the Marine Sediment Quality Standard (MSQS) of China (GB 18668-2002) [29]. Cu, Zn, As, Pb, Cd, and Hg were approximately 0.79-, 0.98-, 0.95-, 1.28-, 3.29-, and 1.33-times higher than their background values, respectively. Compared with other coastal areas, HM concentrations in Daya Bay were generally at an intermediate level (Table 3).

Table 2. HM concentrations (mg/kg) of sediments in Daya Bay, background, and guideline values.

	Hg	As	Zn	Cd	Pb	Cu	Reference
2014 [a]	0.10	7.62	70.81	0.27	25.25	11.33	This study
2015 [a]	0.02	10.53	82.20	0.25	30.31	12.67	
2016 [a]	0.02	7.84	50.94	0.38	33.84	10.41	
2017 [a]	0.02	3.40	49.67	0.19	12.41	7.82	
2018 [a]	0.03	7.31	65.43	0.07	26.17	16.67	
Average [b]	0.04 ± 0.03	7.34 ± 2.55	63.81 ± 13.74	0.23 ± 0.12	25.60 ± 8.13	11.78 ± 3.26	
Background in Daya Bay	0.03	7.70	65.00	0.07	20.00	15.00	[30]
Class I [c]	0.2	20	150	0.50	60	35	
Coefficient of Variation [d]	0.75	0.35	0.22	0.52	0.32	0.28	
TEL [e]	0.13	7.24	124	0.68	30.2	18.7	[31]
PEL [f]	0.7	41.6	271	4.21	112	108	[31]

[a] Average concentration of all samples each year. [b] Average concentration of all samples over five years (average ± standard deviation). [c] Concentration limits of HMs for class I in MSQS of China. [d] Coefficient of variation (CV%) = standard deviation/average. [e] Threshold effect level. [f] Probable effect level.

The threshold effect level (TEL) and the probable effect level (PEL) are widely used to assess HM contamination [32]. In this study, only the As concentration was slightly higher than the TEL, while other HMs were all lower than their TELs and PELs. This result suggested that adverse effects from HMs on the aquatic ecosystem are not significant.

Table 3. HM concentrations (mg/kg) of surface sediments in the Daya Bay and other coastal areas.

Location	Hg	As	Zn	Cd	Pb	Cu	Reference
Hangzhou Bay, China	0.039	10.41	109	0.169	22.6	56.9	[33]
Bohai Bay, China	0.02	8.4	50	0.1	19.4	16.1	[34]
Beibu Gulf, China	0.06	7.82	67.30	0.16	28.00	58.30	[35]
Quanzhou Bay	0.107	5.29	186.7	0.64	66.98	60.81	[36]
Sanmen Bay	0.109	10.0	98	0.11	24	31	[37]
Yueqing Bay	0.07	16.0	139	0.189	37.5	49.7	[38]
Xiangshan Bay	0.106	12.31	120.8	0.15	38.5	36.8	[39]
The Pearl River estuary, China	0.14	22.00	145.56	0.48	50.00	47.89	[40]
Yellow River estuary	0.046	11.42	60.45	0.13	20.86	20.32	[41]
Admiralty Bay, Antarctica	0.02	5.6	59	0.4	4.8	64	[42]
Persian Gulf, Iran	NA	10.84	62.5	0.8	48.3	32.1	[43]

To clarify the variations in HMs in different years, the coefficient of variation (CV%) was estimated to range from 22% (Zn) to 75% (Hg). The CV% values of Hg and Cd were relatively high. Different physicochemical parameters, such as pH, temperature, salinity, and yearly discharges from aquaculture and industries, resulted in large CV% values for Hg (75%) and Cd (52%).

For different years, the concentrations of Hg (0.10 mg/kg), As (10.53 mg/kg), Zn (82.20 mg/kg), Cd (0.38 mg/kg), Pb (33.84 mg/kg), and Cu (16.67 mg/kg) in sediments were highest in 2014, 2015, 2015, 2016, 2016, and 2018, respectively. The temporal variations in HM sediment concentrations are presented in Table 2. As, Zn, Pb, and Cu exhibited similar annual variations. Although the lowest concentrations of these metals in sediments occurred in 2017, the concentrations increased in 2018 possibly due to annual differences in industrial wastewater and domestic sewage discharge around the bay. Compared to those of As, Zn, Pb, and Cu, Hg and Cd exhibited different annual variations. The highest concentration of Hg occurred in 2014, which was followed by a significant decrease in 2015; it remained constant from 2015 to 2018. Except for the highest concentration of Cd found in 2016, the concentration generally exhibited a decreasing trend. Different annual trends for HMs in sediments suggest that the variation in the annual concentration may be influenced by various factors, such as hydrological and meteorological conditions and discharges from different sources.

The spatial distribution profiles of HMs in sediments from Daya Bay are shown in Figure 4. Generally, the lowest HM concentrations were found in the southeast coastal area, whereas the highest concentrations occurred in the northern coastal area. The spatial distribution of HMs in Daya Bay is influenced by point sources, upwelling flow off the Guangdong coast [44], and clockwise circulation patterns of currents. The distributions of Pb and Zn displayed a similar pattern, with high concentrations at the northern sites. Extremely high concentrations of Pb and Zn occurred in Fanhe Harbor (WS23), which is surrounded by cage aquaculture. Yang et al. also found increased Pb and Zn concentrations in sediments from cage aquaculture areas [45,46]. High Pb concentrations were recorded near a nuclear power plant (WS1), which is an important source of HMs in Daya Bay [47]. High Pb concentrations were also recorded in Dapeng Cove (WS27), which is an area known to exhibit cage aquaculture. High concentrations of As were recorded in the eastern (WS24 and WS25) and western (WS11 and WS12) areas of the bay, with the highest concentration being observed at Fanhe Harbor. The concentrations of Cd and Cu exhibited a decreasing profile from north to south. The highest concentrations of Cd and Cu were recorded at the Yaling Cove (WS12), which was heavily affected by local runoff. The highest Hg concentration was recorded in Gangkou Harbor (WS25) possibly due to the domestic sewage discharge. Low HM concentrations were recorded at WS14 and WS19, with the outfall of the first sewage pipeline nearby; this result indicated that the HMs in sediments were not affected by the outfall.

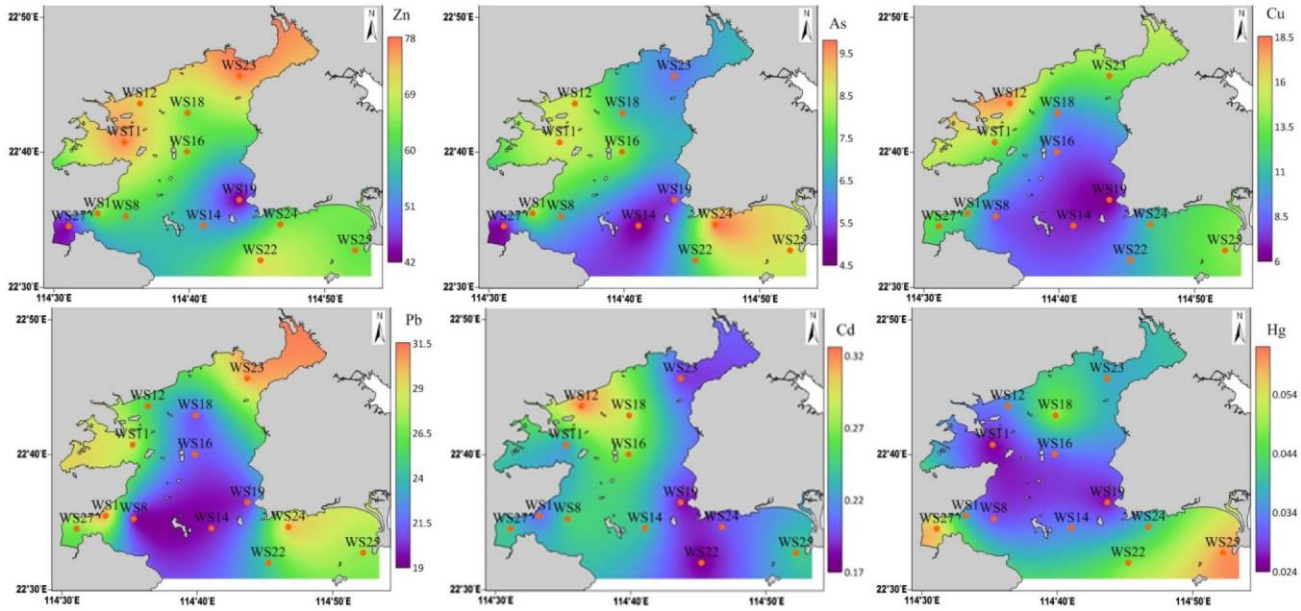

Figure 4. Spatial distribution of HMs in sediments.

3.2. Factors Influencing HMs in the Aquatic Environment

The concentration of HMs in water is significantly affected by the water environment. Owing to the continuous exchange of material and energy in water columns, the physical and chemical conditions, such as salinity, DO, pH, and SS are constantly changing in seawater and affecting the concentration of HMs and other pollutants. In this study, pH was negatively correlated with HM concentrations (Table 4). Since pH affects the chemical properties and existing forms of HMs in seawater, higher pH causes the metal ions in solution to react with OH^- and form hydroxide micro-precipitates, thereby causing a reduction in HM concentration in seawater [48]. However, at a lower pH, HM complexes are easily desorbed from sediments or SS into seawater, thereby increasing HM concentrations in seawater. There was a positive correlation between salinity and three HMs ($p < 0.01$), implying that HMs in seawater are affected by salinity. The results show that the release rate mainly depends on the chemical speciation of HMs, as well as on the concentration of complex ions in seawater. The higher salinity normally results in a higher concentration of the complex ions, which can induce a greater release of HMs from SS and sediments into water [49].

Table 4. Pearson correlation (PC) coefficient matrix of HMs, salinity, dissolved oxygen (DO), suspended solids (SS), pH, and inorganic nitrogen (DIN) in seawater from Daya Bay.

	pH	Salinity	DO	SS	DIN	Hg	Cr	As
pH	1	0.180 **	0.599 **	0.02	−0.325 **	−0.135 *	−0.138 *	−0.142 *
Salinity		1	−0.305 **	0.279 **	0.097	0.312 **	0.327 **	0.322 **
DO			1	0.033	−0.391 **	0.1	0.108	0.102
SS				1	0.155 **	0.120 *	0.111	0.126 *
DIN					1	0.266 **	0.261 **	0.288 **
Hg						1	0.901 **	0.922 **
Cr							1	0.958 **
As								1

* Correlation is significant at the 0.05 level (two-tailed). ** Correlation is significant at the 0.01 level (two-tailed).

There was a positive correlation between SS and the Hg and As concentrations ($p < 0.05$), suggesting that SS may adsorb Hg and As. Therefore, the distribution of these two HMs is highly related to the SS concentration in the water. There was no cor-

relation between DO and HMs, indicating that HMs were less affected by DO. There was a significant positive correlation between inorganic nitrogen and the Hg, As, and Cr concentrations, suggesting that they may originate from common pollution sources.

Pearson correlation analysis of HMs, total organic carbon (TOC), sulfide compounds, oils, and pH in surface sediments was carried out (Table 5). Sulfide was weakly correlated with Cu ($p < 0.05$), and TOC was significantly correlated with Cd ($p < 0.01$) and Hg and Zn ($p < 0.05$), suggesting that these HMs are associated with organic matter and sulfide. The complexation of HMs by organic matter plays an important role in the distribution patterns of HMs in Daya Bay. Apart from Hg and Cd, As was significantly correlated with Zn and Pb ($p < 0.01$) and weakly correlated with Cu ($p < 0.05$), indicating that they had similar sources, as reported in other studies [50]. Hg and Cd were not correlated with other HMs, indicating that Hg and Cd had different sources.

Table 5. Pearson correlation (PC) coefficient matrix of HMs, sulfide, oils, redox potential (Eh), pH, and total organic content (TOC) in the sediments of Daya Bay.

	Sulfide	TOC	Oils	Hg	As	Zn	Cd	Pb	Cu	Eh	pH
Sulfide	1										
TOC	0.689 **	1									
Oils	0.162	0.058									
Hg	0.184	0.269 *	0.085	1							
As	−0.033	0.179	−0.119	0.001	1						
Zn	0.166	0.303 *	0.067	0.104	0.474 **	1					
Cd	0.105	0.325 **	−0.178	0.145	0.067	−0.125	1				
Pb	−0.079	−0.014	0.072	0.048	0.403 **	0.451 **	0.145	1			
Cu	0.254 *	0.033	0.206	0.097	0.300 *	0.462 **	−0.156	0.586 **	1		
Eh	0.104	0.011	0.134	−0.176	0.088	0.073	−0.144	0.131	0.187	1	
pH	−0.023	−0.171	0.024	0.152	−0.192	−0.272 *	−0.011	−0.037	−0.018	0.026	1

* Correlation is significant at the 0.05 level (two-tailed). ** Correlation is significant at the 0.01 level (two-tailed).

3.3. Pollution Assessment of HMs in Sediments

Pollution assessments of HMs in sediments have been carried out widely based on several ecological risk indices, such as the Nemerow pollution index, E^i_r, *RI*, and I_{geo} [20,35,43,51]. The Nemerow pollution index was used to assess HM pollution in sediments over different years. The Nemerow pollution index exceeded 1 in 2018, indicating that HM pollution was "mild" in 2018. The Nemerow pollution index was in the range of 0.7–1 in 2014, 2015, and 2016, indicating that pollution was acceptable during these periods. The Nemerow Pollution Index was also low (i.e., a "clean" condition) in 2017. For the surface sediments, over 80% of the sampling sites were considered "clean", with a small fraction between the "clean" and "mild" pollution levels.

The five-year averages of E^i_r for HMs in surface sediments are shown in Figure 5. The average E^i_r values for HMs were ranked in the following order: Hg (399.69) > Cd (107.71) > As (9.53) > Pb (6.40) > Cu (3.93) > Zn (0.98) > Cr (0.89). The risk levels are presented in Table 1. The average E^i_r values for Hg and Cd were 399.69 and 107.71, corresponding to the extremely high-risk level and relatively high-risk level, respectively. Meanwhile, Hg and Cd accounted for the largest proportion due to the higher toxicity coefficients of Hg (40) and Cd (30) than those of the other HMs [52]. The E^i_r values of other HMs were less than 40, indicating a low-risk level.

The average *RI* values for the sampling sites were ranked as follows: WS27 (834.92) > WS25 (735.41) > WS18 (643.58) > WS22 (577.16) > WS24 (520.7) > WS12 (515.15) > WS1 (485.09) > WS23 (477.88) > WS14 (466.29) > WS16 (449.78) > WS8 (427.37) > WS11 (377.22) > WS19 (356.64) (Figure 5). According to Figure 5, the *RI* value in Daya Bay was mainly influenced by Hg and Cd concentrations, which contributed more than 90% of the *RI*. Daya Bay generally exhibits a relatively high risk. W27, W25, and W18 showed high *RI* values (>600) and were classified as high risk (Figure 5). The *RI* values of the other sites were

between 150 and 300, indicating a relatively high risk. Due to the high toxicity and high proportion of *RI*, Hg, and Cd played a very important role in the ecological risk evaluation in Daya Bay. Tang et al. [13] also found that Cd and Hg pose a very high risk in Daya Bay.

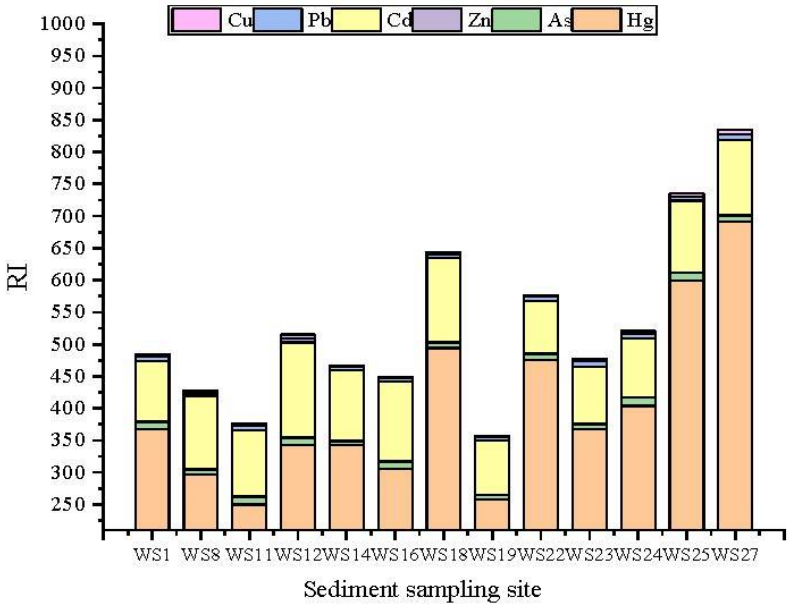

Figure 5. Five-year averages of E^i_r (represented by different colored blocks) and *RI* for HMs in sediments for each sampling site.

The I_{geo} values of HMs are shown in Figure 6. The I_{geo} values of As, Zn, Pb, and Cu were below zero, suggesting that Daya Bay was not polluted by these metals. For Cd, the I_{geo} value was between 1 and 2, suggesting "mild" pollution. For Hg, the I_{geo} value was between 2 and 3, indicating "moderate" pollution. The pollution status of Daya Bay as per the I_{geo} values is consistent with the results provided by the potential ecological risk index (E^i_r).

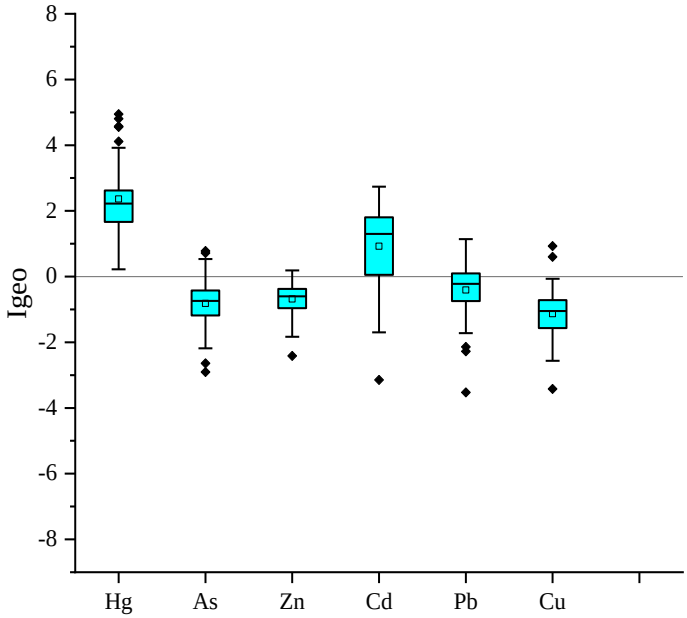

Figure 6. The geoaccumulation index (I_{geo}) of the heavy metals in the surface sediments.

3.4. Source Apportionment of HMs

Water parameters were evaluated using Kaiser–Meyer–Olkin (KMO) and Bartlett's sphericity tests (Table 6). The KMO and Bartlett's results were 0.702 and 1638.451 ($p < 0.05$), respectively, indicating that principal component analysis (PCA) was suitable for reducing dimensionality. Based on the factor analysis, three main components with eigenvalues greater than 1 were determined, accounting for 77.525% of the total variance.

Table 6. PCA results of HM concentrations in seawater.

	F1	F2	F3
pH	−0.090	0.833	0.044
Salinity	0.250	−0.284	0.666
DO	0.198	0.888	−0.106
SS	0.022	0.087	0.883
Inorganic nitrogen	0.267	−0.606	0.104
Hg	0.953	−0.059	0.107
Cr	0.967	−0.057	0.106
As	0.973	−0.068	0.113
Eigenvalue	2.97	1.95	1.28
Variance contribution rate	37.16	24.35	16.02
Cumulative variance contribution rate	37.16	61.50	77.56

Hg, Cr, As, and DIN were highly correlated with the first component, accounting for 37.16% of the total variance. pH and DO were highly correlated with the second component, accounting for 24.35% of the total variance. Salinity and SS were highly correlated with the third component, accounting for 16.02% of the total variance. As of 2020, the Daya Bay petrochemical zone is the largest in China, producing 2 million tons of petroleum and 2 million tons of ethylene per year. Furthermore, 89 projects have been launched in the petrochemical zone, and 63 land-based outlets along the coast of Daya Bay are established, of which 20 are located around the petrochemical zone [53]. The discharge from these outlets into the sea, including domestic sewage and industrial wastewater, might result in an increase in HM concentrations in seawater. Aotou and Xiayong are the two main fishing ports in Daya Bay. Due to the lack of environmental protection measures, the water environment around fishing ports has deteriorated in recent years, and the water quality has not met environmental protection requirements [54]. The main factors affecting the water environment quality of the fishing port are ballast water, tank washing water, and domestic sewage, which might be attributed to HM pollution.

Moreover, the Dan'ao River is the largest river in this area flowing into the sea, starting from Danshui town, Huiyang, and finally flowing into the Baishou Cove. With the economic development of Huiyang, a large amount of urban domestic sewage and industrial wastewater from the electronics and electroplating industries flows along the riverbank into the Dan'ao River, and industrial wastewater usually carries a large number of HMs, such as Cu, Hg, and Cr [45]. In this study, DIN significantly correlated with Hg, As, and Cr (Table 3). Meanwhile, considering the distribution of HMs (Figure 4), the sources of HMs in the first component of the PCA analysis are mainly industrial wastewater and domestic sewage containing nitrogen. Therefore, HMs in seawater might be influenced by anthropogenic inputs, including domestic sewage and industrial wastewater from the petrochemical zone, fishing ports, and rivers.

KMO and Bartlett's sphericity tests were performed to confirm that PCA is suitable for the evaluation of HMs in sediments (Table 7). Three components, accounting for 74.73% of the total variance with eigenvalues higher than 1, were extracted. PC1, PC2, and PC3 were correlated with As, Zn, Cu, Pb, Cd, and Hg. As, Zn, Cu, and Pb were highly correlated with the first component, accounting for 39.28% of the total variance, with loadings greater than 0.71. Cd was highly correlated with the second component, accounting for 19.62% of the

total variance, with a loading of 0.96. Hg was highly correlated with the third component, accounting for 15.84% of the total variance, with a loading of 0.97.

Table 7. PCA results of HM concentrations in sediments.

Component	Initial Eigenvalue			Extract the Sum of the Squares of the Load			The Composition Matrix after Rotation			
	Eigenvalue	% of Variance	Accumulate %	Eigenvalue	% of Variance	Accumulate %	HM	1	2	3
1	2.36	39.28	39.28	2.36	39.28	39.28	Pb	0.81	0.19	0.03
2	1.18	19.62	58.89	1.18	19.62	58.89	Zn	0.77	−0.19	0.10
3	0.95	15.84	74.73	0.95	15.84	74.73	Cu	0.77	−0.27	0.17
4	0.74	12.26	86.99				As	0.71	0.20	−0.18
5	0.45	7.52	94.51				Cd	−0.01	0.96	0.10
6	0.33	5.49	100.00				Hg	0.04	0.10	0.97

The results of PCA, PC, and spatial distributions indicated that Cu, Zn, Pb, As, and TOC have common sources, whereas Cd and Hg have different sources. High concentrations of HMs were mainly observed at Fanhe Harbor and Yaling Cove, which were surrounded by cage aquaculture. Normally, the TOC content is high in sediments from the cage aquacultural areas [55]. Significant positive correlations between the HMs (Cd, Hg, and Zn) and TOC (Table 5) indicated that cage culture might be one of the pollution sources in this study. Meanwhile, discharge from the Dan'ao River and a nearby industrial area was proposed as another source of these metals. The concentrations of As, Zn, Pb, and Cu in sediments are often closely related to waste discharge from outlets [56]. There were dozens of outlets distributed along the coast of Daya Bay. Except for some enterprises discharging sewage through the discharge pipeline, wastewater from other industrial enterprises was discharged directly into the sea. The annual discharge of wastewater from the petrochemical industry in Daya Bay was estimated at 9.2×10^6 m^3. The main pollutants were HMs, ammonia, and petroleum [53]. Therefore, the source of the HMs in the sediments might have been influenced by wastewater discharge from the outlets. According to the high potential ecological risk index and I_{geo} values of Hg and Cd, Hg and Cd may also be influenced by anthropogenic inputs that are different from the sources of Cu, Zn, Pb, and As. Considering the high CV% values of Hg (75%) and Cd (52%) and high concentrations of Hg and Cd found in Gangkou and Aotou Harbors, pollution of Hg and Cd might be attributed to the point sources near the harbors. However, more detailed research is required to assess these sources.

4. Conclusions

HMs in seawater and surface sediment samples in Daya Bay were investigated. The levels of HM concentrations in seawater were relatively low and regarded as class I, based on the SWQS of China. No significant increase in the interannual trend was observed for HMs in seawater. The levels of HM concentrations in sediments were regarded as class I, based on the MSQS of China. Compared with other coastal areas, HM concentrations in Daya Bay were generally at an intermediate level.

Based on the data acquired and the statistical analysis methods, potential pollution sources and risks in Daya Bay were proposed. Pearson correlation analysis revealed that the concentrations of HMs were greatly affected by other parameters, such as pH, salinity, DO, and TOC. The potential ecological risk index (E^i_r) of HMs in sediments indicated a relatively high risk, especially for Hg and Cd. The geoaccumulation indices (I_{geo}) of As, Zn, Pb, and Cu indicated no pollution in Daya Bay, whereas those of Cd and Hg indicated mild and moderate pollution. The principal component, factor analyses, and spatial distribution indicated that Hg, Cr, As, and DIN in water originated from common sources, including domestic sewage and wastewater from fishing ports, runoffs, and outlets. For sediments,

the same sources, including cage aquaculture and waste discharge from outlets, were proposed for Cu, Zn, As, Pb, and TOC.

The present study showed that the HMs in Daya Bay were mostly attributed to anthropogenic activities. Further research on more accurate source apportionment of HMs should be carried out. This study also suggests that effective measures should be taken to control pollutant emissions to achieve sustainable environmental and economic development.

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