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The Spatiotemporal Variation and Historical Evolution of Heavy Metal Pollution in Sediments from the Pearl River Estuary, China

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Abstract: Many tributaries of the Pearl River carry large amounts of terrestrial pollutants into estuarine areas. Heavy metals accumulate in estuarine sedimentary environments, and coupled and changing biogeochemical processes occur in estuarine areas. The results of this study showed that the heavy metal contents in the sediment were the highest near the confluence of the Humen and Jiaomen outlets in 2005 and 2019; they were the second-highest near the remaining outlets, and gradually decreased toward the lower reaches, with high contents on the western shore and low contents on the eastern shore. The heavy metal pollution mainly originated from the Pearl River runoff. The historical evolution of heavy metals in the Pearl River Estuary (PRE) effectively reflected the impacts of pollutant inputs from the river basin as well as industrial and agricultural production and anthropogenic activities in the Guangdong–Hong Kong–Macao Greater Bay Area (GBA). In 2019, the surface sediments were not contaminated with Hg, and the Pb and Zn contents decreased significantly, indicating significant advances in environmental management; however, the Cu and Cd levels still indicated heavy pollution level in the upper reaches.

Keywords: Pearl River Estuary; heavy metal; spatiotemporal variation; historical evolution; marine ecological civilization

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1. Introduction

An estuary area is a zone with intense land–sea interactions. Heavy metals, which originate from industrial and agricultural wastewater, residential sewage, rock weathering and erosion products, and atmospheric precipitation [1], accumulate in estuarine sedimentary environments, and undergo coupled and changing biogeochemical processes in estuary areas [2–4]. Estuarine and marine sediments can be good traps for heavy metals, and these areas have high and stable heavy metal contents, offering natural environmental information related to the basin and recording the impact of anthropogenic activities [5,6]. Therefore, heavy metals are important pollutants that directly affect estuarine and marine environments and have toxic effects on aquatic fauna and flora; through the food chain, heavy metals pollution has a toxic impact on humans [7,8]. The riverways, lakes, oceans, estuaries, and wetlands worldwide are facing heavy metal pollution problems, and due to their accumulation, persistent residual toxicity, and ease of transfer and enrichment in the food chain, heavy metals are harmful to aquatic organisms and human health [9,10], especially heavy metal pollution in estuaries, which is a widely occurring environmental concern [11–16]. Many tributaries of the Pearl River flow through the major industrial and populous cities in the GBA, and with rapid industrialization and economic development, the runoff carries large amounts of terrestrial pollutants into estuarine sea areas [17].

The Pearl River is the third largest river in China, with a total annual average annual runoff of approximately 336 billion cubic meters [18]. The runoff enters the sea through eight outlets, of which the four eastern outlets (Humen, Jiaomen, Hongqimen, and Hengmen) form a trumpet-shaped estuary. In addition, of the four western outlets, Modaomen, Jitimen, Yamen, and Hutiaomen, the Modaomen and Jitimen outlets flow directly into the sea. The water system morphology can be summarized as the confluence of three rivers and diversion into eight outlets [19]. The total annual average amount of sediment transported by the Pearl River is approximately 83.36 million tons, and large amounts of sediment and pollutants are deposited in the estuary [20]. Heavy metal pollution in the PRE has generated widespread concern. Research has been conducted on the spatial distribution of heavy metals in sediments [21,22], pollution status [23,24], existing forms of the elements [25], and analyses of biotoxicity [26], as well as the mechanisms of deposition, migration, and accumulation [27,28]. The PRE is the main load-carrying water body of the Guangdong–Hong Kong–Macao Greater Bay Area (GBA). In 2017, according to the Bulletin on the State of the Marine Environment of Guangdong Province [29], the average quality of the sediments was generally average; the proportion of locations with a status of "good" was only 37.0%, and the main pollutants were Cu, Zn, and Cd, indicating that pollution problems continued to exist in the sedimentary environment. In this study, the results of large-scale surface sediment surveys conducted in the PRE in 2005 and 2019 were used to analyze the spatiotemporal variations, material sources, migration, and transformation of heavy metals in the sediments in recent years. In combination with data on the heavy metal flux into the sea and pollution status, the results of core samples obtained in 2008 were used to study the current status and historical evolution of heavy metal pollution in the study area. These results can provide a scientific basis for marine environment planning and control and can aid in the marine eco-conscious development of the GBA.

2. Materials and Methods

2.1. Sampling

In 2005 and 2019, 165 and 37 surface sediment samples, respectively, were collected from the PRE. The survey covered the four eastern outlets (Humen, Jiaomen, Hongqimen and Hengmen) and the Modaomen and Jitimen outlets, two of the four western outlets, with a sampling area bounded by 113.30° E~114.45° E and 22.70° N~21.70° N. The sampling stations in 2019 extended further into the upper reaches of the estuary and the urban agglomeration in the GBA, reaching 23.00° N (Figure 1). Surface samples from 0–10 cm were collected; each sample fraction was >500 g, and the sandy sediment samples were >250 g. Field samples were collected, placed in sample bags and labeled. In 2008, core samples were collected from the beach of a mangrove wetland on Qi'ao Island in the PRE (113.6276° E, 22.4402° N). The core samples were 198 cm long, and the samples were divided at 2 cm intervals.

2.2. Sample Analysis

Approximately 25 g of each sediment sample was placed in a clean watch glass, baked at 40 ± 2 °C for 48 h, placed in a desiccator to cool, crushed with an agate mortar, and passed through a 180-mesh nylon sieve to obtain sediment samples smaller than a 180-mesh size. In 2005, an X-ray fluorescence spectrometer (Magix Pro PW2440, Eindhoven, The Netherlands) was used to analyze the contents of Cu, Pb, Zn, Cr, and Ni in the surface sediments [30], and the detection limits of Cu, Pb, Zn, Cr, and Ni were 1.0, 1.2, 2.4, 3.6, and 2.0 mg/kg, respectively. In 2008, the heavy metal contents in core samples were determined by inductively coupled plasma mass spectrometry (Finnigan MAT, Bremen, Germany) [31], and the detection limits of Cu, Pb, Zn, Cr, and Ni were 0.08, 0.070, 0.160, 0.070, and 0.003 ng/g, respectively. Based on the results of the present study of heavy metal pollution in the sediments of the PRE, the heavy metal elements investigated were adjusted to Cu, Pb, Zn, Cd, and Hg, among which Cu, Pb, and Cd were analyzed by graphite furnace atomic absorption spectrometry (ZEEnit, Jena, Germany); the detection limits of Cu, Pb, and Cd were 0.5, 1.0, and 0.4 mg/kg, respectively. Zn was analyzed by flame atomic absorption spectrometry (ZEEnit, Germany), the detection limit of Zn was 6.0 mg/kg. Hg was measured by atomic fluorescence spectrometry (KCHG, Beijing, China), and the detection limit of Hg was 0.002 mg/kg [32]. The particle sizes of the surface sediment samples from 2005 and 2019 were analyzed by sieving and laser particle size analysis (Mastersizer 2000 and Mastersizer 3000, Shanghai, China), and the organic carbon (OC) content was measured via the potassium dichromate oxidation reduction capacity method (Brand digital automatic titrator, Shanghai, China) [30]. Standard materials (Offshore Marine Sediment Standards, GBW07314, Institute of Geophysical and Geochemical Exploration, Chinese Academy of Geological Sciences) were used for quality control during the testing process for all the samples to ensure the reliability of the test results, and the range of their average recoveries was 85.2~110.7%.

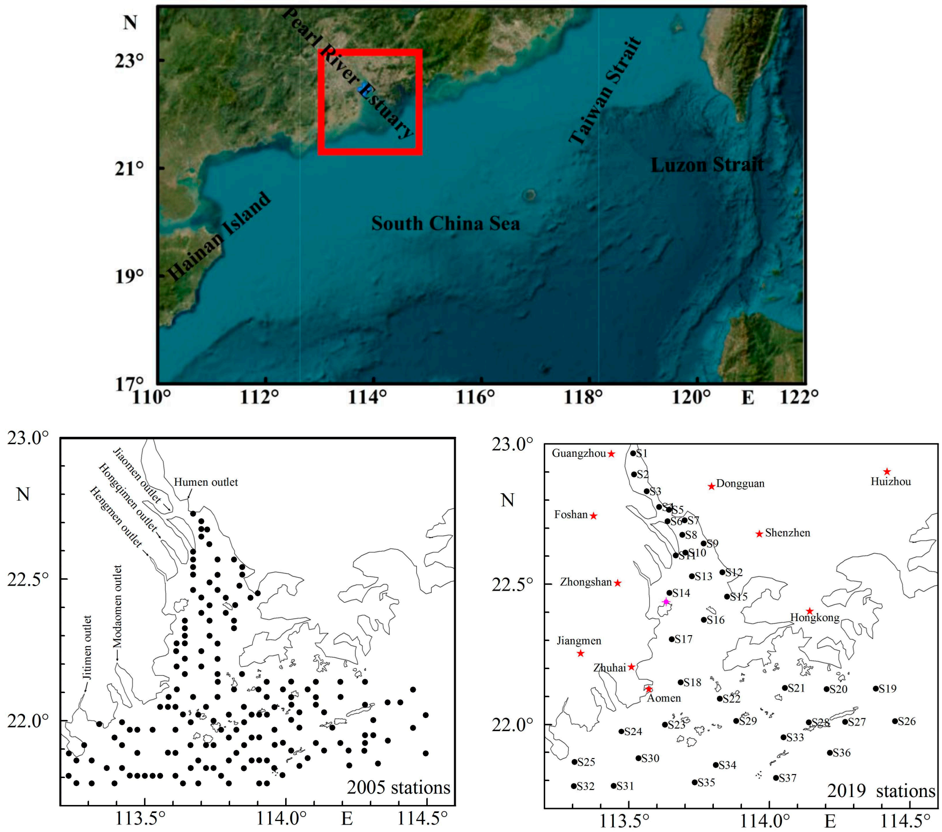

Figure 1. Stations for sediment sampling in the PRE in 2005 and 2019 (● was the surface sediment sations, the 2019 station picture included ✦ core sediment station in 2008).

In the ^{210}Pb analysis of core samples in which ^{209}Po was the tracer, 4 g of dry sediment sample was accurately weighed, added to a known amount of ^{209}Po as a yield tracer, digested with concentrated nitric acid and concentrated hydrochloric acid, and evaporated to dryness. The residue was subsequently leached with dilute hydrochloric acid, and the supernatant was separated via centrifugation. A small amount of hydroxylamine hydrochloride was added to the solution, the pH was adjusted to approximately 2 with aqueous ammonia, and the solution was heated and stirred on a constant-controlled magnetic stirrer to deposit ^{210}Po and ^{209}Po on a silver sheet with an active surface of 12 mm.

After the reaction, the silver sheet was removed, incubated with silver slices, rinsed with purified water and absolute ethanol, dried under an infrared lamp, and subsequently analyzed with an α-energy spectrometer (Alpha Spectrometer, Knoxville, TN, USA) [30].

2.3. Evaluation Methods

Principal component analysis can provide effective information for analyzing the sources of heavy metals in marine sediments and the main factors affecting heavy metal enrichment through dimensionality reduction. The principal components should account for approximately 75.0% of the total variance. Relevant components are those whose eigenvalue is higher than 1.0. The application of varimax rotation of standardized component loadings enabled us to obtain a clear system as a result of the maximization of component loadings variance and elimination of invalid components [33].

The potential harm index is an ecological risk index for aquatic pollution control [34], when the contamination factor or enrichment factor of a single heavy metal $C_f < 1$, a low level of pollution exists; when $1 \leq C_f < 3$, moderate pollution exists, when $3 \leq C_f < 6$, the pollution level is heavy, and when $6 \leq C_f$, the pollution level is severe. The index of geoaccumulation (I_{geo}) is used to evaluate the degree of accumulation level of heavy metals pollution [35]. When $I_{geo} \leq 0$, it indicates a nonpolluted status; when $0 < I_{geo} \leq 1$, it indicates mild pollution; when $1 < I_{geo} \leq 2$, it indicates low to moderate pollution; when $2 < I_{geo} \leq 3$, it indicates moderate pollution; when $3 < I_{geo} \leq 4$, it indicates moderate to high pollution; when $4 < I_{geo} \leq 5$, it indicates high pollution; and when $I_{geo} > 5$, it indicates heavy pollution.

3. Results

3.1. The Spatiotemporal Variation of Heavy Metals in 2005 and 2019

The ranges of the Cu, Pb, Zn, Cr, and Ni contents in the surface sediments of the PRE in 2005 were 12.3~119.3, 25.7~94.5, 88.3~321.2, 32.9~137.8, and 16.2~70.8 mg/kg, respectively, with average values of 36.0, 46.8, 137.2, 82.3, and 37.2 mg/kg, respectively (Table 1). The ranges of the Cu, Pb, Zn, Cd, and Hg contents in the surface sediments of the PRE in 2019 were 7.2~738.2, 23.0~86.4, 67.6~924.1, 0.02~3.16, and 0.040~0.546 mg/kg, respectively, with average values of 84.1, 42.6, 172.6, 0.36, and 0.150 mg/kg, respectively (Table 1). In 2005 and 2019, the heavy metal contents gradually decreased from the upper reaches to the middle and lower reaches, with the lowest values occurring in the outer seas. Extremely high values occurred in the waters near the confluence of Humen and Jiaomen, and the second-highest values occurred in the waters near the remaining outlets. The spatial distribution characteristics (Figures 2 and 3) indicated that the distribution of heavy metals in the surface sediments was significantly affected by runoff. The heavy metal contents of PRE sediments gradually decreased from the waters with the highest turbidity to the upper and lower reaches to the adjacent waters [31]. The Pb, Zn, and Cr contents in the estuary area were approximately twice those in the adjacent waters, and the Cu contents in the estuary area were four times that in the adjacent waters [21]. The heavy metals in the sediments in the PRE mainly originated from river inputs [36]. The heavy metal contents along the western shore of the PRE were high, and those along the eastern shore were low (Figures 2 and 3). The western bank received more pollutant input from tributaries and had different sedimentary conditions to the eastern shore, with more severe heavy metal pollution than that on the eastern shore (Figures 2 and 3) [23,37]. The 2019 survey covered a larger area of the GBA urban agglomerate and the upper reaches of the waters (Figure 1). The Cu contents in surface sediments near the east four outlets and the upper reaches (north of approximately 22.5° N) in 2019 were greater than those in 2005; high Zn contents were present only in the upper reaches of the estuary. The Cu contents in the middle and lower reaches south of 22.5° N in 2019 were greater than those in 2005, and both the Pb and Zn contents in 2019 were lower than those in 2005, with significant reductions in Pb and Zn contents (Figure 2).

Table 1. Heavy metal and OC contents in surface sediments in the PRE.

		Cu	Pb	Zn	Cr	Ni	OC
2005				mg/kg			%
	Variation range	12.3~119.3	25.7~94.5	88.3~321.2	32.9~137.8	16.2~70.8	0.19~1.71
	Average value	36.0	46.8	137.2	82.3	37.2	1.06
		Cu	Pb	Zn	Cd	Hg	OC
2019				mg/kg			%
	Variation range	7.2~738.2	23.0~86.4	67.6~924.1	0.02~3.16	0.040~0.546	0.35~3.26
	Average value	84.1	42.6	172.6	0.36	0.150	1.17

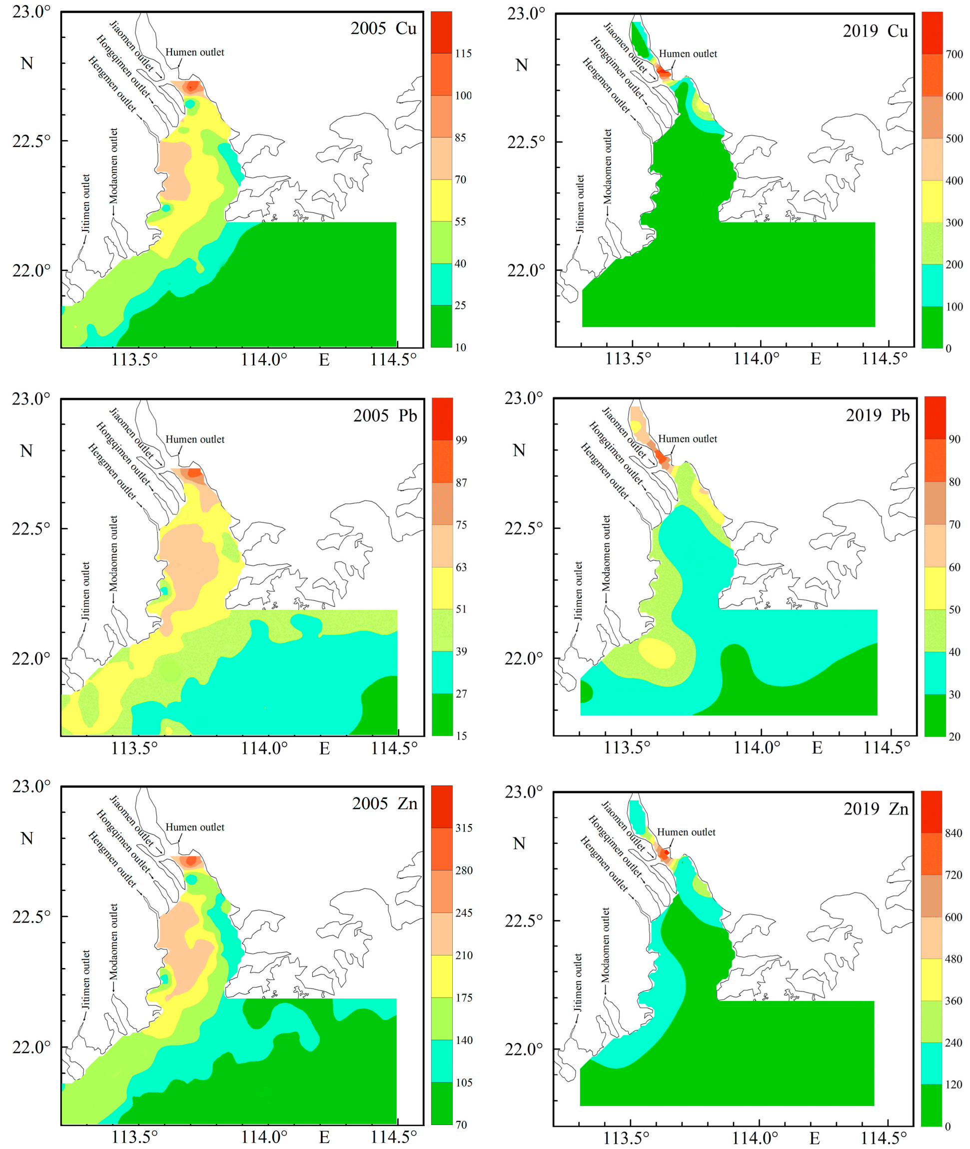

Figure 2. The spatial distributions of Cu, Pb, and Zn in surface sediments in the PRE in 2005 and 2019.

3.2. Historical Change of Heavy Metals Contents

Based on the evolution of heavy metal content in core samples (Figure 4), which rose slowly during 1880~1997, the contents of Cu, Pb, Zn, Cr, and Ni, at 43.3, 36.0, 110.0, 88.1, and 42.0 mg/kg in 1880, increased slowly with fluctuations to 52.0, 56.0, 137.0, 98.6, and 46.6 mg/kg in 1997, respectively, with some fluctuations. The most rapid increase in sediment heavy metal content occurred from 1997 to 2003. In 2003, the contents of Cu, Pb, Zn, Cr, and Ni were 94.0, 85.8, 276.0, 136.0, and 66.1 mg/kg, respectively. During 2003~2005, the heavy metal contents in the sediments decreased slightly; the Cu, Pb, Zn, Cr, and Ni contents decreased to 84.0, 80.7, 251.0, 125.0, and 61.9 mg/kg, respectively, in 2005. The contents of each heavy metal increased again from 2005 to 2008.

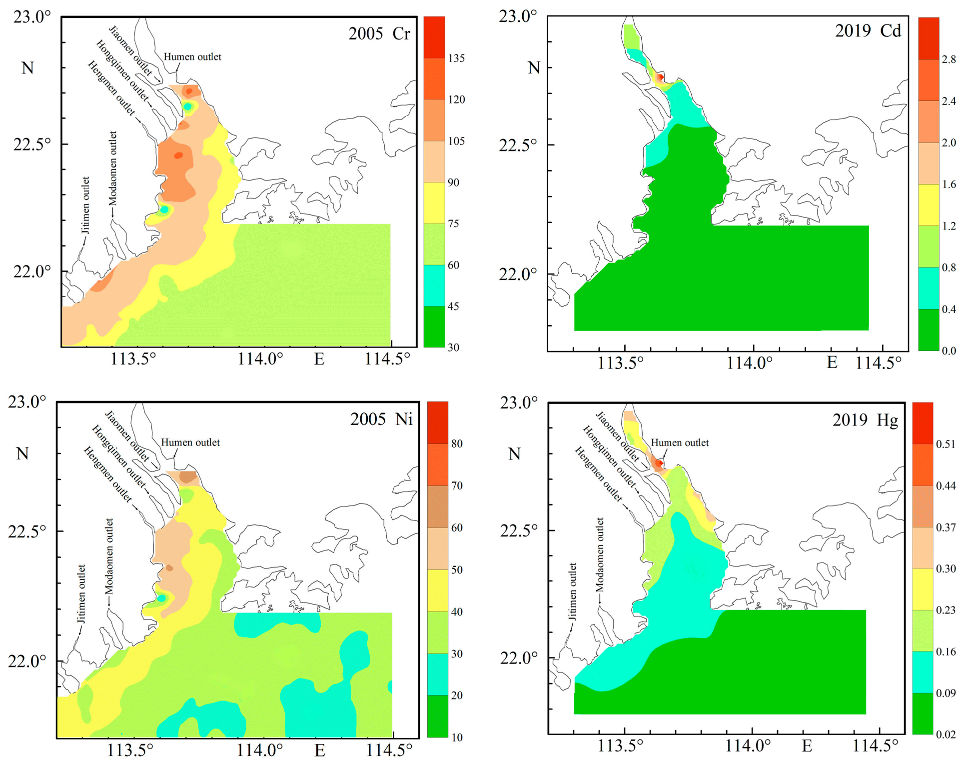

Figure 3. The spatial distributions of Cr and Ni in 2005 and Cd and Hg in 2019 in surface sediments in the PRE.

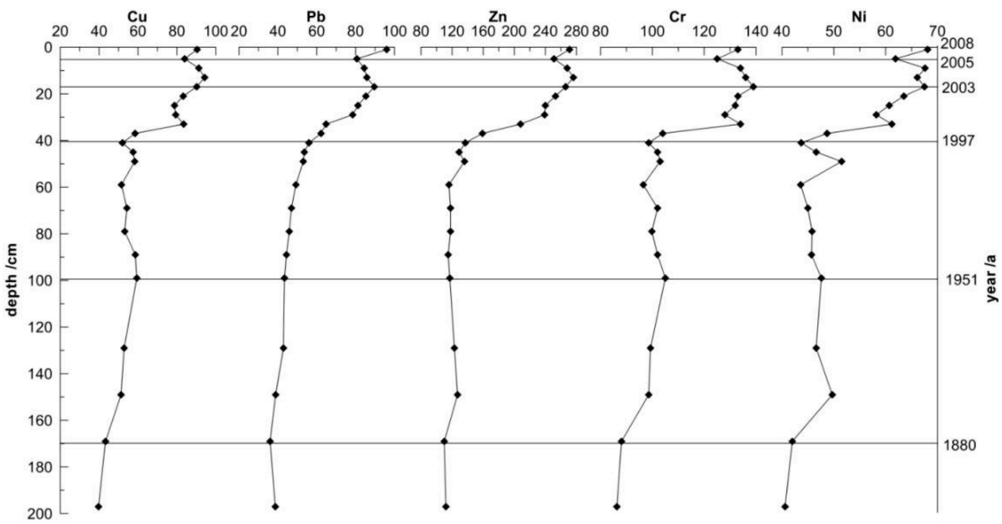

Figure 4. Historical evolution of heavy metal content in core sediment from the PRE.

From 2003 to 2017, the annual fluxes of heavy metals into the sea from the Pearl River and the Shenzhen River decreased significantly overall (Figure 5), but they exhibited a short-term rebound trend during 2005~2008, reached a high value in 2008, and then declined sharply. During 2009~2017, the fluxes of heavy metals into the sea decreased rapidly (Figure 5). The Pb and Zn contents of the surface sediments in 2019 were significantly lower than those in 2005 (Figure 2).

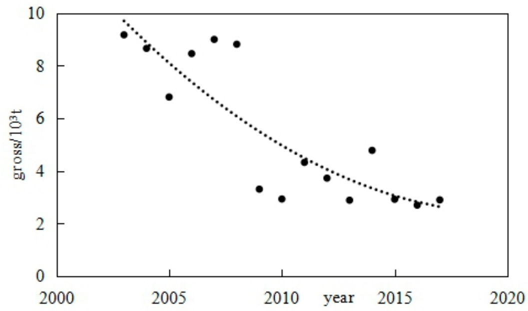

Figure 5. Gross heavy metal pollution in the PRE from 2003 to 2017.

4. Discussion

4.1. Source and Migration of Heavy Metals

SPSS Statistics V19 was used to analyze the correlations between the five heavy metals in the 165 surface sediment samples collected in 2005 and in the 37 surface sediment samples collected in 2019. The minimum correlation coefficient in 2005 was 0.794, while the minimum correlation coefficient in 2019 was also greater than 0.746, indicating significant positive correlations (Table 2) and that heavy metals in the surface sediments were controlled by the same factors and had similar material sources. It was also reported that the contents of five heavy metals, Cu, Pb, Zn, Cd, and Cr, in the PRE sediments were significantly correlated, with correlation coefficients ranging from 0.666~0.894 [26]. Moreover, the results of principal component analysis showed that the first component was the only principal component, with contribution rates of up to 85.750% and 86.267% in 2005 and 2019, respectively (Table 3). The maximum heavy metal contents in the surface sediments in 2005 and 2019 were observed at the confluence of the Humen and Jiaomen outlets, and the heavy metal contents decreased toward the middle and lower reaches to the outer seas, reaching their second-highest values in the waters near the remaining outlets (Figures 2 and 3). This pattern indicated that the heavy metals mainly originated from terrestrial runoff input and were significantly affected by anthropogenic activities. Relevant studies have also shown that the concentrations of the heavy metals Cu, Zn, Cd, Cr, Ni, and Pb in the sediments of the PRE were the highest in the waters near the estuary. In addition to being influenced by industrial and agricultural production processes, Pb was also affected by factors such as natural weathering and atmospheric deposition [23,38]. Thus, the significant reduction observed in Pb could have been influenced by the promotion of lead-free gasoline and the popularity of electric vehicles.

Table 2. Correlation coefficients of environmental factors in surface sediments in the PRE in 2005 (n = 165) and 2019 (n = 37).

		Cu	Pb	Zn	Cr	Ni	OC
2005	Cu	1					
	Pb	0.926	1				
	Zn	0.923	0.926	1			
	Cr	0.878	0.794	0.821	1		
	Ni	0.947	0.888	0.925	0.871	1	
	OC	0.704	0.760	0.637	0.597	0.719	1
		Cu	Pb	Zn	Cd	Hg	OC
2019	Cu	1					
	Pb	0.776	1				
	Zn	0.916	0.811	1			
	Cd	0.808	0.746	0.887	1		
	Hg	0.808	0.878	0.851	0.881	1	
	OC	0.822	0.896	0.827	0.808	0.811	1

Table 3. Summary of the computed results for the principal component analysis.

2005		2019	
	The First Component		The First Component
Cu	0.974	Cu	0.921
Pb	0.946	Pb	0.916
Zn	0.952	Zn	0.950
Cr	0.904	Cd	0.921
Ni	0.966	Hg	0.938
OC	0.802	OC	0.926
Contribution rate/%	85.750	Contribution rate/%	86.267

The variation ranges of the OC contents in 2005 and 2019 were 0.19~1.71% and 0.35~3.26%, respectively, with average values of 1.06% and 1.17%, respectively (Table 1). The OC contents increased slightly in recent years, as evidenced by the high OC content in the upper reaches, the gradually decreasing OC content in the middle reaches, and the low OC content in the outer seas. Furthermore, the OC content along the western shore was greater than that along the eastern shore, which paralleled the distribution characteristics of the heavy metals (Figures 2, 3 and 6). In 2005 and 2019, the heavy metal contents in surface sediments were significantly correlated with the OC contents, with the correlation coefficients in 2005 and 2019 reaching 0.597 and greater than 0.808, respectively (Table 2), indicating that sedimentary OC and heavy metals had the same source [22]. On the other hand, sediments with high OC contents were prone to heavy metal adsorption and accumulation [39].

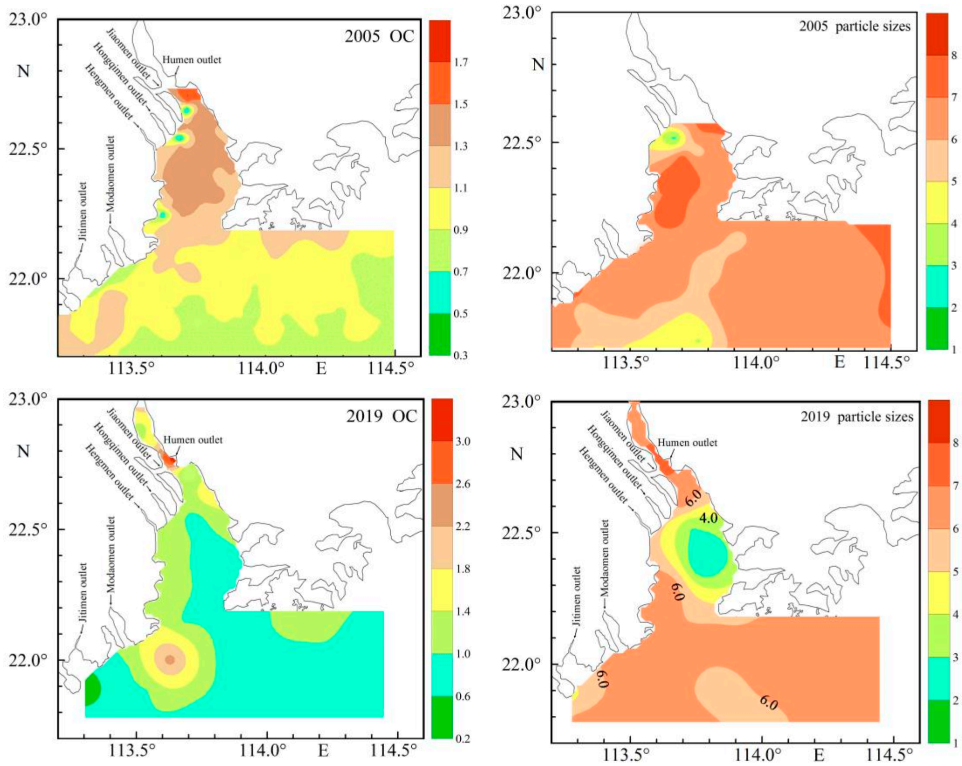

Figure 6. The spatial distributions of particle sizes and OC in surface sediments in the PRE in 2005 and 2019.

The distribution patterns of heavy metals and OC in the surface sediments described above can be mainly attributed to the following reasons: (1) the average annual runoff in the upstream of the survey area and the Jiaomen and Humen outlets accounted for 18.5% of the total runoff in the Pearl River, and this runoff flowed through major cities in the

GBA, such as Guangzhou, Shenzhen, Foshan, Dongguan, and Huizhou, which have strong industrial production and large populations (Figure 1). The heavy metals and organic matter discharged in wastewater from industrial production and domestic sources greatly impact the sedimentary environment. In addition, the semi-enclosed topography and tidal water characteristics of the estuary area impede the transport of pollutants to the outer sea, causing the contents of both heavy metals and OC to be highest in the waters near the outlet. Similarly, heavy metal pollution in the PRE was affected mainly by high-intensity industrial activities, with the superimposed effects of agricultural production and input from adjacent waters [40]. (2) The flux of heavy metals into the sea via the PRE is closely related to runoff, with the upper reaches receiving input from the river and the lower reaches receiving input from the upper reaches flowing to the outer sea; these inputs determine the distribution characteristics of heavy metals [41]. The upper reaches of the surveyed waters received total runoff from the Dongjiang River and some runoff from the Beijiang and Xijiang Rivers; the suspended sediment carried by the runoff reached the outlet waters where there was strong differentiation resulting in mechanical sedimentation. With the mixing of water bodies and changes in physical and chemical environmental conditions, chemical deposition increased, and heavy metal and OC deposition and burial led to a gradual decrease in the concentrations of both from the upper reaches to the lower reaches. (3) The survey waters covered the four eastern outlets and the Modaomen and the Jitimen outlets among four western outlets; the runoff and sediment transport volumes of these six outlets accounted for approximately 88% of the total volume delivered by the Pearl River into the sea and were mainly distributed on the western shore of the PRE. Therefore, the waters on the western shore were affected by more runoff and related pollutants than those on the eastern shore [23]. In addition, affected by the Coriolis force and coastal current, the Pearl River runoff mainly migrates southwestward throughout the year, further causing the western shore waters to receive more terrestrial substances [22]. (4) The PRE is dominated by runoff and tidal currents, with the tide flowing along the eastern shore during flood tide and out along the western shore during ebb tide. The eastern shore is dominated by erosion, and the western shore is dominated by sedimentation. The surface sediments in 2005 and 2019 had particle sizes in the ranges of 1.85~7.75ϕ and 1.80~7.27ϕ, with mean values of 6.16ϕ and 6.25ϕ, respectively. The sediments in the upper reaches of the survey waters were mainly clayey silt, those in the middle reaches and the western shore were mainly clayey silt and silt, and those in the lower reaches and eastern shore were mainly silt and sandy silt (Figure 6). The fine-grained components of the sediments in the middle and upper reaches and the western shore waters accounted for a large proportion of the total sediments, had favorable sedimentary environments, and were prone to heavy metal adsorption [23,27,42]. (5) The high heavy metal and OC concentrations in the waters near Modaomen were particularly obvious, mainly because the Modaomen outlet receives runoff from the Xijiang River and accounts for 28.3% and 33% of the total runoff and sediment transport in the Pearl River; these values were the highest among those for the eight outlets of the Pearl River. The river feeding the Modaomen outlet flows through major industrial and agricultural production cities in the GBA, such as the western shore cities of Foshan, Jiangmen, Zhongshan, and Zhuhai (Figure 1). The large-scale development and rapid economic growth of regional cities from the late 20th century to the early 21st century led to an increase in pollutant discharge into the sea [22].

4.2. Historical Evolution of Heavy Metals Pollution

Based on the potential harm index method and index of geoaccumulation, the regional background values of Cu, Pb, Zn, Cr, and Ni were 16.1, 35.2, 94.3, 69.3, and 30.3 mg/kg, respectively [29]. The C_f of Cr was <1 during 1880~1997, indicating a low level of pollution. The C_f of Pb, Zn, and Ni was greater than 1 and less than 2, exhibiting moderate pollution. Only the C_f of Cu was >3, exhibiting a moderately heavy pollution. According to the geoaccumulation index, the I_{geo} values of Pb, Zn, Cr, and Ni were ≤ 0 during 1880~1997, which indicated no pollution, and the Cu was at low to moderate pollution due to $1 < I_{geo} \leq 2$

(Table 4). During 1997~2003, the pollution levels of the five heavy metals increased by 1.4~2.0 times, corresponding to high pollution; furthermore, the Pb, Zn, and Ni values increased to moderate pollution levels. The I_{geo} values of Pb, Zn, Cr, and Ni were <1, and at low pollution levels, the maximum I_{geo} values of Cu was 1.97, still <2 (Table 4). Other research results have shown that heavy metal pollution in the PRE increased significantly in this period, with Cu and Pb pollution increasing rapidly [23,30]. These increases were mainly due to the rapid societal and economic development and rapid development of regional industries around the Pearl River Delta, which led to an increase in the volume of pollution discharge. The total amount of heavy metals carried into the sea by runoff correspondingly increased [39,43,44], and the heavy metals were deposited mainly in the estuary and adjacent areas. Therefore, the heavy metal contents in the sediments increased significantly. Although the pollution associated with each heavy metal decreased slightly in 2003~2005, it increased again in 2005~2008.

Table 4. Contamination factors (C_f) of individual heavy metal and geoaccumulation index (I_{geo}) for heavy metals in sediments.

			Cu	Pb	Zn	Cr	Ni
Core samples	C_f	Variation range	2.47~5.86	1.02~2.72	1.17~2.93	0.51~0.82	1.33~2.25
		Average value	4.14	1.75	1.87	0.67	1.76
	I_{geo}	Variation range	0.72~1.97	−0.55~0.86	−0.36~0.96	−0.27~0.42	−0.16~0.58
		Average value	1.42	0.15	0.23	0.10	0.21
2005	C_f	Variation range	0.76~7.41	0.73~2.68	0.94~3.41	0.47~1.99	0.53~2.34
		Average value	2.24	1.33	1.45	1.19	1.23
	I_{geo}	Variation range	−0.97~2.30	−1.04~0.84	−0.68~1.18	−1.66~0.41	−1.49~0.64
		Average value	0.34	−0.23	−0.12	−0.37	−0.33
2019			Cu	Pb	Zn	Cd	Hg
	C_f	Variation range	0.45~45.9	0.65~2.45	0.72~9.80	0.01~15.8	0.24~3.21
		Average value	5.22	1.21	1.83	1.8	0.88
	I_{geo}	Variation range	−1.75~4.93	−1.20~0.71	−1.07~2.71	−3.91~3.40	−2.67~1.10
		Average value	0.34	−0.40	−0.10	−1.12	−1.16

From 2005 to 2019, the average C_f and I_{geo} of Pb decreased from 1.33 to 1.21 and −0.23 to −0.40, respectively, indicating a moderate pollution level and no pollution. Similarly, the average C_f of Zn was 1.83, still exhibiting a moderate pollution level in 2019 (Table 4). Cu exhibited an increasing trend and a high pollution level overall in the upper reaches north of 22.5°N, and the maximum C_f and I_{geo} of Cu were 45.9 and 4.93 in 2019, respectively, and significantly greater than 7.41 and 2.30 in 2005 (Table 4), but a decreasing trend occurred in the middle and lower reaches. In addition, the background concentrations of Cd and Hg were 0.20 and 0.170 mg/kg, respectively [45]. The maximum C_f and I_{geo} of Cd reached 15.8 and 3.40, respectively, indicating a heavy pollution level (Table 4). Overall, the surface sediments were not polluted with Hg in 2019. The Cu and Cd pollution in the surface sediments in 2019 was mainly near the confluence of the Humen and Jiaomen outlets, their upper reaches, and the western shore waters near the remaining outlets (Figures 2 and 3). These patterns were basically consistent with the main heavy metal pollutants (namely, Cu and Cd) in the Guangzhou and Foshan Basins and the upper reaches of the PRE in 2007 [26].

In summary, the area near the PRE, which is the main load-carrying water area of the GBA, has experienced rapid regional population growth and economic development. The historical records of heavy metal contents in the core samples and the results of surface sediment surveys in 2005 and 2019 effectively reflected the process and extent of the impact of anthropogenic activities on heavy metal pollution in the areas around the PRE and in the basins. The amounts of heavy metals discharged into the sea and the heavy metal pollution in sediments have gradually decreased since 2008, indicating that the GBA has achieved significant advances in environmental management.

Different methods were used in different laboratories to measure the concentration of heavy metals in sediments, and standard materials were used to ensure the quality and reliability of data. The test results were reliable, but further comparative analysis among different laboratory results would be needed. Although the survey covered the four eastern outlets and the Modaomen and Jitimen outlets in the PRE, it did not cover the middle and upper reaches of the four western outlets; therefore, the estuarine sedimentary environment in the GBA must be further studied. The Cu and Cd levels in the upper reaches of the four eastern outlets still indicated heavy pollution, which should be given attention.

5. Conclusions

The scope of the 2019 survey covered more upper reaches in the PRE, and the Cu and Zn contents in the surface sediments near the four eastern outlets and the upper reaches in 2019 were greater than those in 2005; however, the Pb and Zn contents in the lower reaches in 2019 were both lower than those in 2005, with significant reductions in Pb and Zn contents.

In 2005 and 2019, the heavy metal contents in the sediments of the PRE gradually decreased from the confluence of the Humen and Jiaomen outlets to the middle and lower reaches of the estuary, respectively, with high contents on the western shore and low contents on the eastern shore. The second-highest contents were found near other outlets. The heavy metals of the sediments was mainly from Pearl River runoff.

The heavy metal content in the sediments from the PRE increased slowly in the 100-plus years from 1880 to 1997, increased rapidly from 1997 to 2003, decreased slightly from 2003 to 2005, and then increased again from 2005 to 2008. The annual flux of heavy metals into the sea reached a high value in 2008 and then sharply declined. In 2019, the Pb and Zn contents were much lower than those in 2005, but the Cu content showed an increasing trend. The historical evolution of heavy metals in sediments was influenced mainly by anthropogenic activities and industrial and agricultural production. In 2019, the Cu and Cd contents in the sediment were extremely high at the confluence of the Jiaomen and Humen outlets, resulting in a high level of pollution.

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