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Extent and Sources of Heavy Metal Pollution from Discharging Rivers in the Bohai Region, China

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Abstract: Studies have investigated heavy metal (HM) contamination in the Bohai Sea, but primarily in seawater and associated sediments, or in single rivers. For the first time, 31 major rivers discharging into the Bohai Sea were analyzed, along with 27 uniformly distributed coastal seawater samples and selected invertebrates. The elements measured were As, Cd, Cr, Cu, Ni, Pb, V, and Zn. We calculated the 'geo-accumulation index', the 'metal enrichment factor', and the 'contamination factor', coupled with the 'pollution load index', and our findings suggested low-grade HM pollution, although two conspicuous associations of elements were found to stand out in particular: One is a combination of As, Cu, Cr, and V in seawater samples that may indicate pollution from intensive ship traffic. The other shows a significant pattern of Cr, Pb, and Zn in water samples from rivers discharging between Yantai and Weihai on the Shandong Peninsula at the south edge of the Bohai Sea. This is primarily a farming area, with a moderate share of industrial enterprises. Investigations including fertilizers and pesticides point to agricultural practices and textile printing/chrome tanneries as the causes of contamination. Overall, a significant decline was found in the HM load in the rivers, apart from those discharging into the Yellow Sea section.

Keywords: Bohai Sea; heavy metal pollution; river discharge; risk assessment; fertilizers; pesticides

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1. Introduction

The Bohai Sea lies in a semi-enclosed bay in Northern China, off the northwest Pacific. Major rivers bring abundant nutrients into the sea, making this region a natural spawning and feeding ground for fish [1]. However, considerable amounts of wastewater and pollutants like heavy metals, plastic waste, and fertilizers are also discharged into the bay. As more and more industrial companies have been set up in the regions around Bohai Bay in recent years, it has become one of the most polluted marine areas in China. According to the current general understanding, the main suppliers of trace metals found in the waters of the Bohai Sea, aside from atmospheric inputs and biodegradation, are the discharging rivers, while other pathways have relatively little impact [2]. It is estimated that the marine-based pollution has contributed about 20%, while the effect of land activities accounts for 80% [1]. According to a press release in 2015, nearly 2.8 billion tonnes of sewage and 700,000 tonnes of solid waste are spewed into the bay every year, and its pollution accounts for almost half of the total discharged into the country's offshore waters [3]. Moreover, there is heavy ship traffic throughout the year, and the Liao and Shuangtaizi Rivers carry significant loads of crude oil that is pumped extensively north of Liaodong Bay. In this context, three major oil spills occurred in the Bohai Sea from 2005 to 2011 [4]. All of this has negatively impacted the sustainable development of the Bohai Sea, and this threat continues into the future.

In recent years, a number of authors have investigated heavy metal contamination in and around the Bohai Sea. Gao and Chen [5] analyzed six HMs in sea and river sediments at 42 stations, finding obvious anthropogenic influences, albeit relatively low as compared to other marine coastal areas. Investigations of surface sediments in Liaodong Bay indicated that Cu, Pb, Ni, and As pose environmental risks to the area, at low-to-medium priority [6]. Pb and As were mainly attributed to anthropogenic sources, and all other HMs were attributed to parent rocks. Li et al. [7] summarized the advancement in sediment metal pollution studies in China, finding the contamination status to be serious in coastal areas, with Liaodong Bay as the worst, followed by Bohai Bay, Laizhou Bay, and the central basin of the Bohai Sea. Kuang et al. [8] investigated the HM contamination in water bodies and riverbed sediments in the flood and dry seasons along the Yang River. All concentrations were found to be low and less than the threshold values, whereby the moderate pollution downstream was much higher than in the upstream. A further review article was presented, investigating 3171 sediment samples for eight major HMs, indicating a slight increase in concentrations between 1980 and 2017 [9]. Generally, higher concentrations were measured in Bohai Bay and the central Bohai Sea. Ding et al. [10] researched the spatial distribution and risk assessment of HMs in surface sediments along the Hebei coast. They found that most measured concentrations met China's marine sediment quality criteria. However, a few stations showed moderate-to-strong pollution with Cd and Hg, and about 25% of all sites had a high ecological risk even at those lower concentrations. From the decrease in concentrations from near-shore to offshore, they deduced strong influences by anthropogenic activities. Han et al. [11] analyzed the concentrations of six common HMs in surface sea water and sediments along the Tianjin coastal region. They ascertained Cu to be high in the surface seawater, and Cd was identified as the main contaminating metal in the sediments.

Zhang et al. [12] investigated the spatial and temporal distribution trends and risk assessment of HMs in the Bohai Sea's waters from 2013 to 2017. From the eight common HMs, Pb was found to be the main pollution factor, while Hg and Cd were the main potential ecological risk factors due to their high toxicity. Li et al. [13] researched the occurrence and risk of HMs in the Liao River protected area and found moderate pollution for all common HMs, with increased background values of 25–50% in water and sediments. Gao et al. [2] provided a comprehensive review paper with recordings of a broad spectrum of HM concentrations in seawater, sediments, and organisms from a variety of authors. In summary, they found very high metal concentrations in the western Bohai Bay and the northern Liaodong Bay, especially on the coast near Huludao, which is polluted by industrial sewage from the surrounding areas. Liang et al. [14] investigated the flux and source–sink relationship of HMs and As from 12 sampling sites and water samples from 37 rivers across the Bohai Sea and the north Yellow Sea, concentrating on atmospheric deposition and riverine discharge. It was determined that the atmosphere is the main pathway for Pb, whereas riverine discharge dominates the input of Cr, Cu, Zn, Cd, and As into the marine environment. Thereby, Liaodong Bay is assumed to be a sink for HMs, while Bohai Bay and Laizhou Bay act as sources. Seasonal and spatial variations in the HMs in surface seawater and six rivers of Liaodong Bay were recently investigated by Guo et al. [15]. The pollution factor of HMs was in the order Pb > Zn > Cu > Cd, where the total degree was relatively high in summer and autumn after the rainy season and lower in winter and spring.

In 2018, the northern Chinese port city of Tianjin unveiled a three-year action plan (2018–2020) to curb pollution in the Bohai Sea. A document released by China's Ministry of Ecology and Environment mandates that measures are taken to ensure that about 73 percent of Bohai Sea's coastal waters are fit for human contact in 2020. According to reports, the government has addressed issues with factories, agriculture, urban runoff, and ship traffic, and has targeted its campaign primarily on outflows and rivers as one of the main delivery routes of the pollution. These facts, along with several previous reports on the extent of pollution, with some rather contradictory results, prompted these investigations. Our primary objective was to determine the extent, distribution, and potential sources of HM contamination in all streams flowing into the Bohai Rim, and to ascertain how the situation has changed from previous years. For this purpose, for the first time, the loads of all discharging rivers were analyzed almost simultaneously for HM contents and for element associations that could be related to possible sources in their catchments. In this way, more detailed insights into the extent and distribution of pollution throughout the Bohai Rim were obtained. In support of this primary goal, further measurements were conducted on river sediments, seawater in the respective estuaries, and also selected invertebrates, so as to determine whether potential contaminants had already entered the food chain. Finally, comparisons with previously recorded literature data allowed conclusions to be drawn about changes over time, particularly after the 'three-year plan' came into effect. The investigations carried out in this study focused for the first time on the simultaneous acquisition and consecutive analysis of the HM contents of all major rivers discharging into the Bohai Sea. The goal was to determine whether measures taken in recent years have been successful in reducing the discharge of wastewater into rivers flowing into the Bohai Sea.

2. Study Area

The Bohai Sea is China's largest coastal bay, subdivided into three major sections, namely, Liaodong Bay in the north, Bohai Bay in the west, and Laizhou Bay in the south (Figure 1). The Bohai Rim, with 66 harbors, is not only one of China's most populous areas but also a highly industrialized region, with manufacturing, fisheries, salt production, and oil extraction. The sea has an average water depth of about 18 m, with a maximum of about 80 m [16]. There are more than 40 rivers flowing into the Bohai Sea, among which the Yellow River, Hai River, Luan River, Shuangtaizi River, and Liao River are the five main ones. The average discharge of all of the rivers and streams is about 61.8 million m^3/a [17]. The area investigated includes the entire Bohai Rim and the adjacent northern coast of the Shandong Peninsula from Yantai to Weihai, a section that is assigned to the Yellow Sea. This area, flanking the Bohai Strait, is characterized by industrial and agricultural activities as well, and it is therefore closely linked to the Bohai Rim. All rivers examined and all sampling points are depicted in Figure 1.

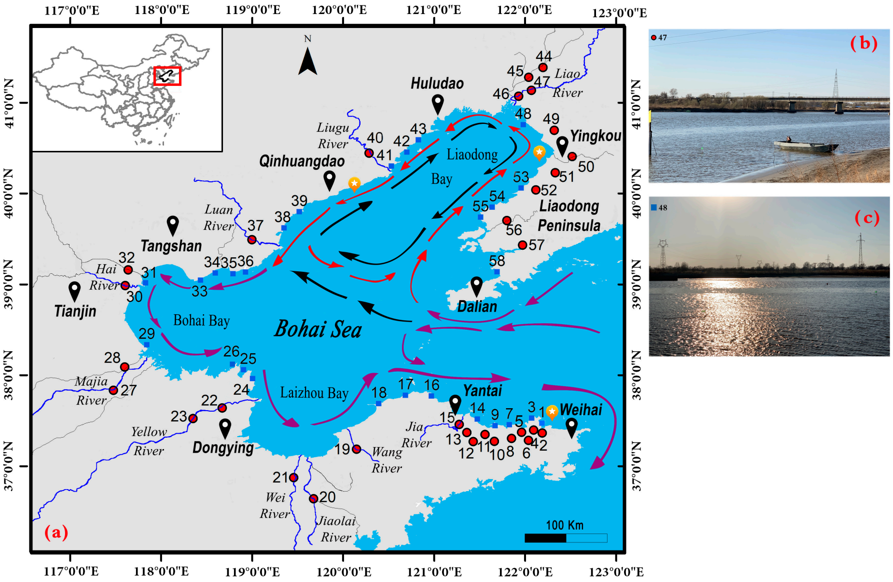

Figure 1. (**a**) Sketch map of the Bohai Sea. Sampling locations are indicated by numbers. Red round dots mark sampling points for river water, partially in connection with sediment samples. Rectangular blue dots denote seawater sampling spots. Yellow stars denote the breeding places of analyzed invertebrates. Flow patterns according to Li et al. [18]. Red arrows = summer currents, black arrows = winter currents, purple arrows = currents through summer and winter. (**b**,**c**) Scattered oil slicks along the banks of the Liao River and floating on its surface.

3. Materials and Methods

3.1. Sample Collection and Preparation

We collected water samples from all major discharging rivers (31), samples of river sediments, invertebrates, and uniformly distributed coastal seawater samples (27) along the entire Bohai Rim, including the aforementioned section of the Yellow Sea in the south. The field investigations took place from 3 to 6 April 2019, to cover not only potential industrial pollution but also possible fertilizer and pesticide inputs of the farming community, which usually take place in early springtime. There was no precipitation for two weeks in the entire area; thus, an overall balanced drainage could be expected for the investigated region. Sampling began in the southeast near the city of Weihai and ended at the city of Dalian in the north. The analyses of all samples were conducted directly after the field work.

The sampling sites for river waters and sediments were chosen primarily to be located close to the river's mouth, so as to cover almost all possible inputs of industrial sites along the respective rivers but without the influence of the sea where they discharge. In other words, we took river samples from fresh water, not from brackish waters. Samples were located with GPS information and supplemented by the main industrial sites in their catchment area (Table S1). In parallel, we collected coastal seawater samples along the entire Bohai Rim to learn about the fluctuations in HM pollution from coastal industry, as well as offshore sources like ship traffic and others. From each sampling site of the river and seawater samples, two liters of surface water was collected three times in deeply prewashed brown bottles, and wading sampling was executed according to the Chinese national standard (HJ/J 91-2002) [19]. The bottles were acidified with nitric acid (pH = 2), sealed after sampling, and delivered to the laboratory immediately after sampling. In the laboratory, the river and seawater samples were analyzed using a NexION 350D 'Inductively Coupled Plasma Mass Spectrometer' (ICP-MS) (Perkin Elmer, Waltham, MA, USA). Before the analyses, the instrument was carefully calibrated, and the calibration solutions and samples were measured for the calculation of uncertainties. The ICP was calibrated using appropriate Perkin Elmer Pe-Pure Spectroscopy-grade standards to ensure accuracy. All samples were analyzed three times, and the average values were recorded each time. Replicate analyses of the blank, standard, and samples were carried out to achieve the highest level of precision (accuracy: 3% RSD). The water samples were filtered (0.45 µm mesh) and diluted up to 10 times with HNO3 (1%, *v*/*v*) before analysis. We aimed at quantification of the dissolved part of trace elements, excluding the suspended matter. The elements analyzed in the river and seawater samples were arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), vanadium (V), and zinc (Zn).

Fluvial sediments were taken three times from several locations where fine-grained clays and silt could be found (∼0.45 kg each). These were stored in polythene bags for transport. The HM contents in the fluvial sediments were determined by X-ray fluorescence (XRF) using a 'NITON XL3t GOLDD+' (Thermo Scientific, Waltham, MA, USA) analyzer calibrated against certified standards (CRM) [20–22]. The handheld Niton XL3 analyzer has excitation filters that can optimize analyzer's sensitivity to various elements in different matrices. It has three test modes: the mining mode, soil mode, and 'test all' mode. In our case, the 'test all' mode obtained more stable values with 4 filters in the main range, low range, high range, and light range, with a duration of 30 s each and 120 s in total. The detection limits are provided in Table 1. As the concentrations of Cd, Cr, and V in our samples were below the sensitivity of the measuring device, the elements analyzed by dry weight were As, Cu, Ni, Pb, and Zn. The strong correlations between the XRF and ICP-MS of these elements (As (0.868), Cu (0.999), Ni (0.903), Pb (0.996), and Zn (0.834)) showed high detection accuracy with a 95% confidence interval [22,23]. All samples were naturally air-dried in the laboratory to remove the diluting influence of moisture, and shell particles were also removed. They were then ground in an agate mortar and passed through a 2 mm mesh to remove the influence of large non-soil particles before the measurements. All samples were subsequently measured six times in the laboratory, and the final results were averaged.

Table 1. Detection limits of HMs for the NITON XRF device.

Elements	As	Cu	Ni	Pb	Zn	Cd	Cr	V
LOD of a typical soil matrix (ppm)	7	13	30	12	10	12	22	25

Additionally, we processed different types of invertebrates, such as sea snails and sea cucumbers from several locations, to analyze the bioaccumulation of the respective trace metals. The species (three each) were obtained from local fishermen working in aquaculture near Qinhuangdao, Yingkou, and Weihai. The locations of the breeding sites are marked in Figure 1. The transport and analysis procedures were conducted in accordance with the Chinese national standard GB17378.3-2007 [24]. The digestions were performed in a Multiwave PRO (Anton-Paar, Graz, Austria) microwave reaction system. Thereby, all soft tissues were considered for the sea snails, and the whole body without the digestive tract was considered for the sea cucumber. A homogenized sample (0.2 to 0.5 g) was transferred into a PTFE (polytetrafluoroethylene) vessel after being smashed and sieved through a 0.45 µm mesh. Then, 8 mL of HNO_3 was added to the vessel, and it was sealed in a graphite heater at 100 °C for 60 min. Finally, the solutions were put into the Multiwave PRO again for 5 min at an initial temperature of 80 °C, heated up in steps of 5 °C/min until 180 °C, and then kept stable for 15 min. Finally, the nitric acid was removed from the acid-catching meter and evaporated to a nearly dry condition. After cooling and washing, the sample was moved to a volumetric flask and diluted to a final volume of 50 mL using ultrapure water. Blank digestion was performed in the same way. Further detailed descriptions for all analytical procedures concerning the pretreatment of sediments, and of both fluviatile and seawater samples, can be found in the work of Zhou et al. [25]. The elements analyzed in sea cucumbers and sea snails were As, Cd, Cr, Cu, Ni, Pb, V, and Zn.

3.2. Estimation of the Degree of Heavy Metal Pollution in Sediment Samples

To evaluate possible anthropogenic fractions of heavy metal contents in the sampled fluvial sediments, widely accepted indices such as the 'geo-accumulation index' (Igeo), the 'metal enrichment factor' (EF), and the 'contamination factor' (CF) coupled with the 'pollution load index' (PLI) were applied. Descriptions and formulae are provided in Table 2.

Table 2. Indices used for estimating grades of HM pollution and anthropogenic influences.

Indices	Descriptions	Equations	References
Geo-accumulation index (Igeo)	Uses the relation of measured values to defined background values to rank the intensity of HM pollution into seven classes.	$\mathrm{Igeo} = \log_2 (C_n/1.5\ B_n)$ where Cn = measured HM concentration; Bn = geo-chemical background.	[26]
Metal enrichment factor (EF)	Normalizing the observed elements and their background values based on an aluminum (Al) standard, followed by a ratio procedure to determine whether the pollution is of natural origin or manmade.	$\mathrm{EF} = \frac{X_s/Al_s}{X_b/Al_b}$ Values between 0.5 and 1.5 refer to natural sources, and those above 1.5 to human activities.	[27]
Contamination factor (CF)	Ratioing the concentration of each metal in the sediment samples by its background value, without normalization. This is a monitoring index of HM enrichment in the sediments over a period of time.	$\mathrm{CF} = \frac{C_{metal}}{C_{background}}$ Results are scaled into four classes.	[28]
Pollution load index (PLI)	Defined as the nth root of the multiplications of the CF of metals, providing an evaluation of the overall toxicity status of the corresponding sample.	$\mathrm{PLI} = [\mathrm{CF}_1 * \mathrm{CF}_2 * \mathrm{CF}_3 \ldots * \mathrm{CF}_n]^{\frac{1}{n}}$ Values of 1 indicate a baseline level of pollution; those above 1 indicate progressive deterioration.	[29]

The abovementioned indices require background values from natural, uncontaminated sources for ratioing against Al values and index calculations (Table 3). We used values of Entisols measured from soils derived from rock types dominating the entire Bohai Rim [30]. Additional background values of Al needed for the EF approach only are not included in the Entisols, so we had to revert to generalized values from China, published by CNEMC-1990 [31].

Table 3. Background values (mg/kg) used to calculate the Igeo, EF, and CF indices.

	As	Cd	Cr	Cu	Ni	Pb	Zn	Al
CNEMC [1]	7.3	0.071	44.0	24.4	23.1	47.5	86.1	**97,100**
Entisols [2]	**9.4**	**0.09**	**63.0**	**22.2**	**28.9**	**21.4**	**69.7**	--

Notes: [1] CNEMC [31]. [2] Entisols [31]. Values in boldface were used for calculation. -- means the value is not available.

There are no specific guidelines defined by the Chinese authorities for river waters or river sediments. In this case, we utilized US-EPA values. Guidelines for river sediments are given as TEC values by the US-EPA [32] (Table 4a). Those for seawater are separated into two grades of suitability by GB 3097-1997 [33] (Table 4b). The guidelines for river waters are provided in two different US-EPA criteria, the CCC and the CMC [34] (Table 4c). For the HMs in the river waters, a 'hazard quotient' (HQ) was calculated referring to standard US-EPA procedures [35]. Thereby, the HM concentrations were set in relation to reference values provided by the US-EPA's CCC guideline values [34]. A quotient less than or equal to 1 indicates that the HM in question can be considered to have negligible impact. HQs greater than 1 are a simple statement of whether an exposure concentration exceeds the reference concentration. To classify the HM concentrations of sea cucumbers and sea snails, the GB 18421-2001 guidelines for shellfish [36] were employed (Table 5).

Similarities in the patterns of distribution and strength of the measured heavy metals may indicate possible common sources. Therefore, the 'agglomerative hierarchical clustering' (AHC) method was deployed to work out possible associations of elements in seawater and river water samples [37]. The elements were grouped into clusters based on their proximity to one another and calculated by Ward's minimum variance method [38]. As the elements were paired into binary clusters, the newly formed ones were grouped into larger clusters until a hierarchical tree was formed.

Table 4. (**a–c**) Guideline values for HM concentrations in fluvial sediments, seawater, and river water.

a: Guideline Values (mg/kg) for HM Concentrations in Fluvial Sediments								
[1] US-EPA	**As**	**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**V**	**Zn**
TEC	9.79	0.99	43.4	31.6	22.7	35.8	--	121
b: Guideline Values (μg/L) for Dissolved HM Concentrations in Seawater								
[2] GB 3097-1997	**As**	**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**V**	**Zn**
Grade 1	20	1	50	5	5	1	29 *	20
Grade 2	30	5	100	10	10	5	--	50
c: Guideline Values (μg/L) for Dissolved HM Concentrations in River Water								
[3] US-EPA	**As**	**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**V**	**Zn**
CCC	150	0.25	11	9	52	2.5	15	120
CMC	340	2	16	13	470	65	50	120

Notes: US-EPA, (2002) [1]. TEC: Threshold effect concentrations below which harmful effects are unlikely to occur. [2] GB 3097-1997 * Value from GB 11607-89 [39]. Grade 1: Suitable for marine fishery waters and marine nature reserves. Grade 2: Suitable for aquaculture areas, sea bathing areas, and recreational areas. US-EPA [34] [3]. CCC (Criterion Continuous Concentration) is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect. CMC (Criteria Maximum Concentration) is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect. -- means the value is not available.

Table 5. HM concentrations (mg/kg, wet weight) in sea cucumbers and sea snails compared to the guidelines for shellfish.

[1] **GB 18421-2001**	**As**	**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**V**	**Zn**
Grade 1	1.0	0.2	0.5	10	--	0.1	--	20
Grade 2	5.0	2.0	2.0	25		2.0		50
Grade 3	8.0	5.0	6.0	50	--	6.0	--	100
Sea cucumber-Q	0.37 ± *0.04*	0.05 ± *0.003*	0.19 ± *0.02*	1.41 ± *0.23*	0.06 ± *0.003*	0.05 ± *0.003*	0.02 ± *0.001*	2.70 ± *0.36*
Sea snail-Q	***13.91*** ± ***0.8***	**3.96** ± ***0.49***	0.33 ± *0.04*	**36.86** ± ***2.61***	0.18 ± *0.02*	**0.15** ± ***0.01***	0.05 ± *0.003*	***151.43***± ***8.53***
Sea cucumber-W	1.05 ± *0.14*	0.06 ± *0.003*	0.28 ± *0.03*	1.31 ± *0.21*	0.20 ± *0.02*	0.05 ± *0.003*	0.08 ± *0.004*	3.81 ± *0.41*
Sea snail-W	***8.15*** ± ***1.35***	**2.72** ± ***0.36***	0.41 ± *0.05*	***91.20*** ± ***6.56***	0.55 ± *0.08*	**0.24** ± ***0.007***	0.06 ± *0.003*	***104.24*** ± ***7.37***
Sea cucumber-Y	0.90 ± *0.11*	**0.28** ± ***0.008***	0.07 ± *0.004*	1.16 ± *0.19*	0.15 ± *0.01*	0.03 ± *0.002*	0.07 ± *0.004*	5.84 ± *0.71*

Notes: [1] GB 18421-2001. Grade 1: Suitable for marine fishery waters, marine aquaculture areas, nature reserves, and industrial water areas directly related to human consumption. Grade 2: Suitable for general industrial water areas. Grade 3: Suitable for port waters and marine development operation areas. Values exceeding grade 1 are displayed in boldface. Values exceeding grade 2 are depicted in boldface and underlined. Values exceeding grade 3 are in boldface, underlined, and italicized. Q, W, and Y indicate the three locations near Qinhuangdao, Weihai, and Yingkou (Figure 1) where the invertebrates had been bred in aquaculture. Measured concentrations are given as the mean ± standard deviation. -- means the value is not available.

4. Results

4.1. River Sediments

The measured concentration ranges of the river sediments were 6.7–10.1 mg/kg for As, 25.9–47.2 mg/kg for Cu, 38.4–58.6 mg/kg for Ni, 17.6–40.6 mg/kg for Pb, and 33.0–249.4 mg/kg for Zn (Figure 2). The mean concentrations of As, Pb, and Zn met the US-EPA [32] guidelines for fluvial sediments, apart from one outlier each measured for the Yuniao River (10). Half of the Cu and all of the Ni samples exceeded the US-EPA guidelines by up to 20% and 40%, respectively (Table 4a). In general, sediments from rivers draining into the Yellow Sea section showed significantly higher HM values as compared to rivers discharging into the Bohai Sea. Furthermore, the PLI was calculated and added to the figures of the respective graphs (Figure 2).

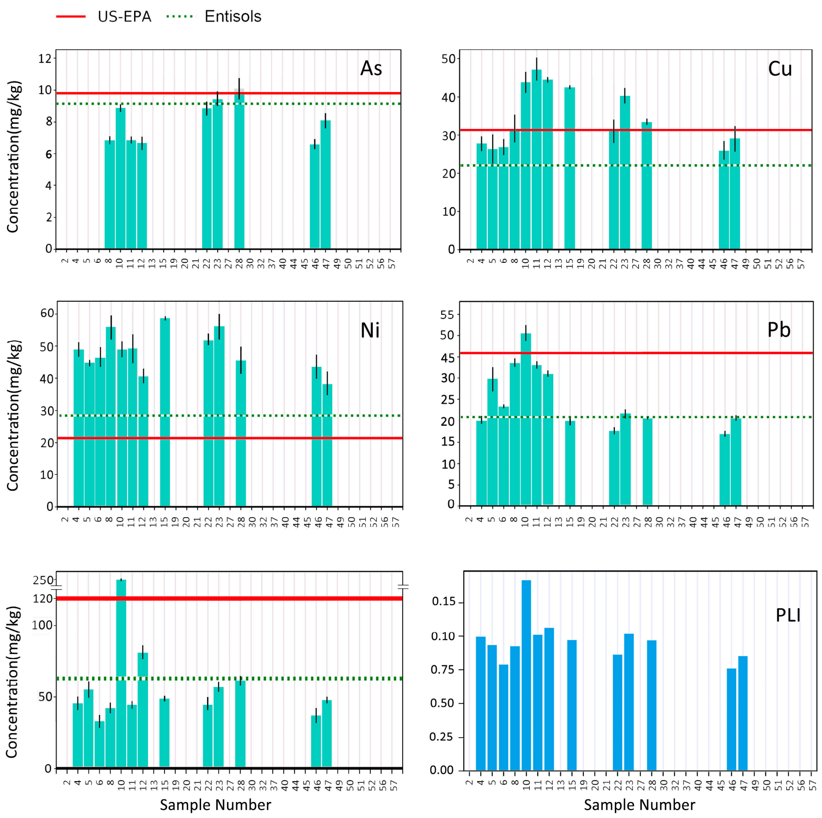

Figure 2. HM concentrations in fluvial sediments, including error bars (based on the standard deviation). Further displayed are calculations of the respective PLI values (for guideline values, see Table 4a).

4.2. Seawater

The concentration ranges of heavy metals in littoral seawater were 8.43–13.5 µg/L for As, 0.03–6.37 µg/L for Cd, 1.68–4.55 µg/L for Cr, 3.56–22.64 µg/L for Cu, 0.25–23.71 µg/L for Ni, 0.15–7.20 µg/L for Pb, 4.59–7.48 µg/L for V, and 16.43–123.5 µg/L for Zn (Figure 3). The results of the seawater samples express that Cu in particular does not meet the Chinese GB 3097-1997 [33] grade 1 and 2 standards (Table 4b), exceeding both standards in nearly all samples by a factor of 2 to 3. The Cd values exceeded grade 1 in some samples taken between Yantai and Weihai (3, 7 and 14). Ni and Zn exceeded grade 1 of GB 3097-1997 in most samples [33]. Ni, Pb, and Zn further showed one to several significant outliers in littoral seawater samples in Laizhou Bay and Bohai Bay (17, 29, 31). The values of Cr were far below the grade 1 standards. The values for As and V were below the Chinese grades 1 and 2 of GB 3097-1997 [33] but slightly increased in comparison to standard mean concentrations in the world's oceans (3–5 µg/L) [40,41].

Figure 3. HM concentrations of seawater samples, including error bars (calculated with the standard deviation). For guideline values, see Table 4b.

4.3. Invertebrates

For the selected invertebrates, the HM concentrations of As, Cd, Cr, Cu, Pb, and Zn are displayed in comparison to the respective Chinese standards (GB 18421-2001) [36] in Table 5. The sea cucumbers generally met the stricter grade 1 level for all HMs. For the sea snail species, only Cr met the grade 1 level. Cd and Pb exceeded grade 2, while As, Cu, and Zn exceeded even the grade 3 level. The sea snail species taken near Qinhuangdao showed the highest values for Zn, As, Cd, Cu, and Pb, while the ones taken from seawater near Weihai showed the order Cu, Zn, As, Cd, and Pb.

4.4. River Waters

The measured concentrations of the river waters were 0.17–12.5 µg/L for As, 0.03–1.25 µg/L for Cd, 1.80–58.77 µg/L for Cr, 0.04–22.9 1µg/L for Cu, 2.34–244.1 µg/L for Ni, 0.20–12.77 µg/L for Pb, 0.30–9.22 µg/L for V, and 12.60–730.2 µg/L for Zn (Figure 4). The analytical values of the river water samples showed a far less balanced distribution as compared to the seawater samples. As, Ni, and V met the US-EPA guidelines [34] for the stricter CCC level (Table 4c), with only one outlier for Ni in the waters of the Hai River (number 30 = 244.01 mg/kg). Increased values of Cd and Ni were found in the Yangting River and a related sewer (5, 6). Cd, Pb, Cr, Cu, and Zn showed significantly increased values for rivers discharging between Yantai and Weihai (1–15). The Cd and Pb values remained below the moderate CMC guidelines, while the Cr, Cu, and Zn values exceeded those criteria. The mean levels of the elements were somewhat comparable to those of the seawater samples, but with significantly decreased values for some rivers, namely, the Jialai, Yellow, and Liao, discharging into Laizhou Bay and Liaodong Bay. Cr, Cu, Pb, Zn and, allusively, Cd depicted a similar distribution of HM concentrations, showing a clear separation between rivers discharging into the Bohai Rim and those discharging into the adjacent Yellow Sea section. In this context, it should be mentioned that the median values of HMs of those rivers with the highest drainage capacity—namely, the Yellow River (22, 23), Hai River (30), Luan River (37), Raoyang River (44, 45), and Liao River (46, 47), sampled at several locations—showed by far the lowest values for all elements measured, whereby the downstream values were expectably higher than the upstream values).

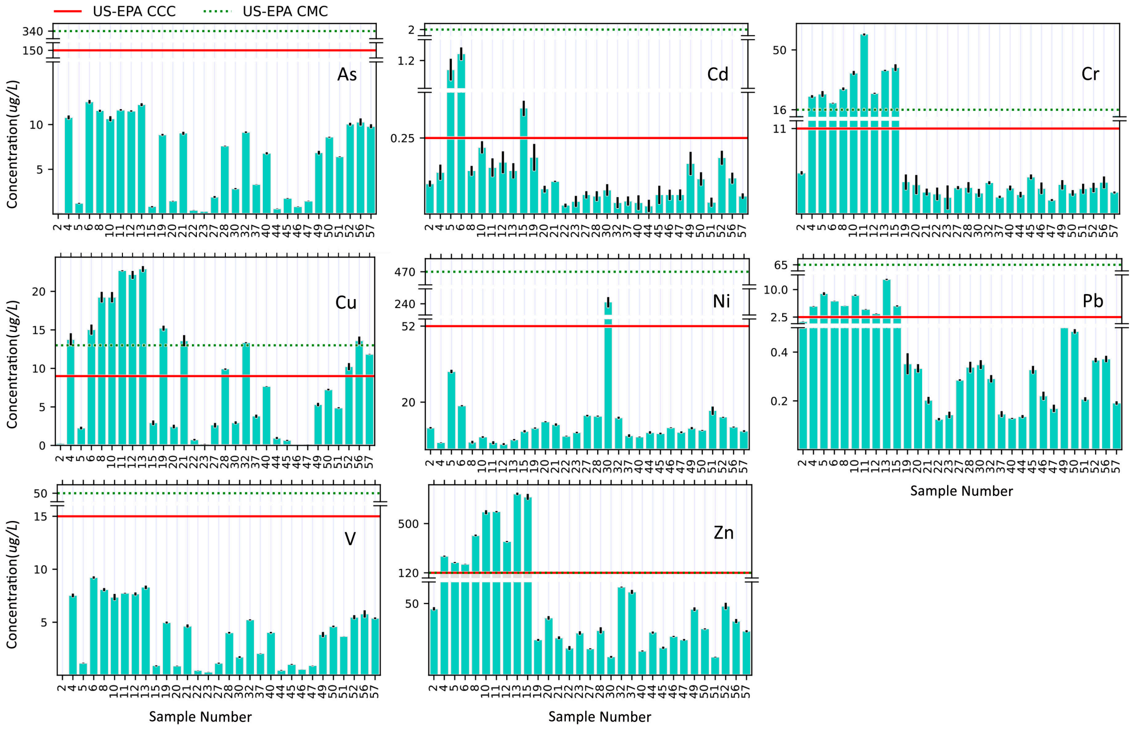

Figure 4. HM concentrations of river water samples, including error bars (based on the standard deviation). For guideline values, see Table 4c.

5. Discussion

5.1. River Sediments

To assess the extent of the heavy metal contamination, three different indices were calculated, namely, Igeo, EF, and CF. All of them displayed a comparable ranking of values for the intensity of the pollution by the individual elements, in the following order: Ni > Cu > Pb > As = Zn (Figure 5). According to the Igeo, the contamination with heavy metals was balanced between classes 0 and 1, ranging from unpolluted to moderately polluted. The lowest values were measured for As, Zn, and Pb; only Ni and (slightly) Cu reached class 1. Concerning the results of the EF index, each heavy metal under investigation exceeded the 1.5 barrier that separates the polluted from the non-polluted level. The third index, the CF, ranked As and Zn as class 1 (low contamination) and Cu, Ni, and Pb as moderate contaminants. The PLI, as based on the CF, depicted well-balanced values between 0.75 and 1, thus indicating a baseline level of pollution. Only the Yuniao

River (10) showed a value somewhat above 1, primarily due to increased values of Pb and Zn. The slight tendency of increased values of Cu, Pb, and Zn for those rivers draining into the Yellow Sea (2–15) was reflected more clearly in the river water samples. Comparing the results of all indices, it can be stated that just a moderate surplus of the heavy metal contents in the fluvial sediments around the Bohai Sea is not of natural origin but attributable to human activities.

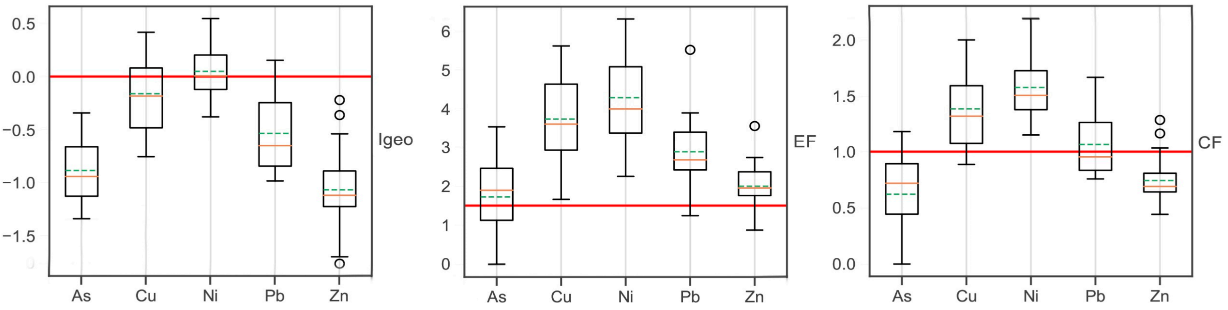

Figure 5. Common presentation of the calculated Igeo, EF, and CF indices. All reveal a comparable low-to-moderate pollution of fluvial sediments by HMs (For background values, see Table 3).

5.2. Seawater

The readings of the seawater and river water samples were further subjected to AHC analyses (Figure 6a,b), as the derived element associations can point to the respective sources of the HMs. Considering the seawater samples, two major clusters emerged (Figure 6a): One comprised As and V, with further associations to Cr and Cu. The second cluster included Ni and Zn, along with Cd and Pb. Cu is a ubiquitous element that is used for steel and alloy production as well as marine antifouling paints and is often naturally contaminated with As. Furthermore, V, Ni, Cu, As, and Cr are the most abundant trace metals in heavy fuel oils or crude oil, which are used to power large cargo ships [42]. Thus, there is a direct release of Cu by the sides of cargo ships and an indirect contamination of V > Ni > As > Cr via the atmosphere through the combustion of crude oils in the ships' marine diesel engines [43]. Although cargo ships with open-loop scrubbers release less HMs into the atmosphere, they flush even more of these elements directly into the seawater, where the V and Ni values are proportional to the sulfur content of the fuels used [44]. Considering the heavy maritime traffic in the Bohai Sea, with a throughput of 4.47 million TEU (twenty-foot equivalent standard container unit turnover volume) for the Tianjin Port in the first quarter of 2021 [45], it can be imagined that the increased quantities of the aforementioned heavy metals released into the bay's waters originate not solely from the local steel and alloy production, but also from ship traffic. On the other hand, Ni, as a main component of crude oil, in our case, was not associated with the As, V, Cr, and Cu cluster by using the AHC method, even though when the ratio of V to Ni is higher than 0.7 (in our case, ~0.6) it is always considered to be influenced by shipping emissions [46].

The second cluster, the combination of Cd, Ni, Pb, and Zn, points to several processes, especially battery production and alloy electroplating [26,47,48]. Excluding the values of the seawater samples taken along the Yellow Sea section (1–16) from the AHC calculations, a Cr, Zn, Ni cluster emerged, connected to Cd and Pb, similar to the results derived for all river values. Only a few subtle outliers of these elements, found on the east coast of Laizhou Bay (17, 18), in the entire Bohai Bay (25–31), and on the southeast coast of Liaodong Bay (53–55), exceeded the SEPA grade 1 and 2 guidelines.

Comparing the measured HM values with the mean values collected by several authors between 2003 and 2012, as compiled by Gao et al. [2], the Cr and Zn values were largely unchanged, while Cd and Pb were substantially lower (by factors of three and five, respectively), and the values for As and Cu were increased by a factor of four.

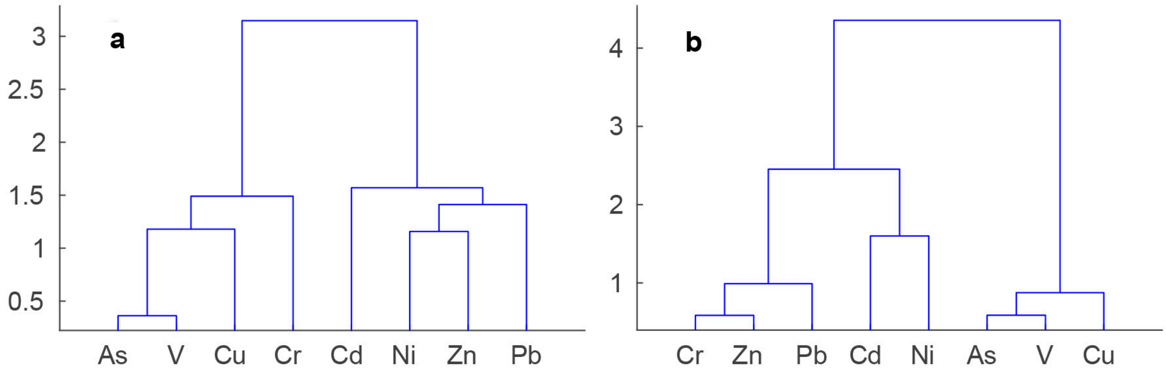

Figure 6. Hierarchical dendrograms emphasizing clusters of associated heavy metals in the (**a**) seawater and (**b**) river water samples.

5.3. Invertebrates

We further analyzed two types of invertebrates (sea snails and sea cucumbers from aquaculture) to determine the extent to which HMs have reached the food chain. In particular, the sea snails are a sentinel for trace metals, primarily due to their bioaccumulation and biomagnification capacity [49]. They have limited mobility and uptake trace metals from the seawater and the sediments. Although not of statistical relevance, the sea snails especially were characterized by strongly excessive HM values, which coincided with the increased concentrations of Cu and Zn found in all seawater samples. In relation to the specified guidelines for shellfish, the HM load in sea cucumbers was far lower than that in sea snails, probably due to the existence of more efficient detoxification/excretion mechanisms [50]. The highest concentrations in sea snails were found for Zn > As > Cu > Pb, followed by Cd. A comparison of these HM concentrations with those of the seawater showed a good agreement with regard to the increase in Cu, Pb, and Zn and the low Cr values. The relatively high As concentrations in the sea snails were not reflected. A comparison of the concentrations found in the sea snails with the corresponding river inputs at the Weihai site (Yellow Sea section of the Bohai Rim) showed a good agreement for Cu, Zn, Pb, and Cd, but As and Cr depicted controversial behavior. For the Qinhuangdao site, the Luan River could be a source of the increased Zn values. Finally, it can be stated that compared to the mean values measured for invertebrates during the years 1999–2008 [2], the values of As, Cu, Ni, and Zn remained largely unchanged, while the contents of Cd, Cr, and Pb are now significantly lower.

5.4. River Waters

One of the aims of our investigations was to determine whether the measures taken by the respective authorities to contain river pollution have been effective. As there are no simultaneous measurements of all rivers flowing into the Bohai Sea from previous years, values from literature databases (China National Knowledge Infrastructure (CNKI)) for the period 2010–2016 were used for comparison with our measurements [51]. The following table compares the median values from the database with our measured median values, excluding our samples taken between Yantai and Weihai (Table 6). Apart from an increase in the As values and stagnating Ni values, all of the elements measured in this study showed lower values than the cumulative median values recorded in previous years, by a factor of around 2 to 3. From our perspective, it can therefore be concluded that the measures of the 3-year initiative appear to have been successful.

Table 6. Median values of HM concentrations (μg/L) measured in river waters inside the Bohai Rim (19–57), accumulated from 2010–2016 and this study.

Element	As	Cd	Cr	Cu	Ni	Pb	V	Zn
CNKI 2010–2016	5	0.1	8	7	10	1	--	50
This study (2019)	6.4	0.06	3.3	4.9	9.1	0.3	3.7	29

Note: -- means the value is not available.

A further goal was to identify potential sources responsible for the HM pollution by the use of AHC calculations. Thereby, two significant clusters were found: As, Cu, V and Cr, Zn, Pb, with close connections to Cd and Ni (Figure 6b). The cluster of As, Cu, and V was also present in the seawater samples, but without Cr, and the values were generally lower for rivers draining into the Bohai Sea in contrast to those discharging into the Yellow Sea, indicating moderate pollution. There was a highly significant association of observable patterns of As, Cu, and V concerning all rivers investigated. There were uniform increases in concentrations for the rivers Wang (19) and Wei (21) discharging into Laizhou Bay, for the rivers Zhangweixin (28) and Yongding (32) draining into Bohai Bay, and for the rivers Liugu (40), Daliao (49), Daqing (50), Xiongyue (51), Fudu (52), Fuzhou (56), and Anzi (57) discharging into Liaodong Bay. The patterns of As, Cu, and V were nearly identical and, thus, strongly suggest a common origin. A comparable dissemination was not evident in the seawater samples or in the river sediments. For the seawater samples, the heavy ship traffic can be held co-responsible, while for the river water samples fossil fuel combustion on land and industrial processes such as metal processing come into question (Table S1). However, this is not a satisfactory explanation for the consistently uniform pattern of the values of the three elements for all rivers, as there is certainly no homogeneous distribution of the respective industries throughout the entire Bohai Rim. A further attempt to approach this issue may be found in the natural environment. Areas with higher levels of As in China are usually associated with naturally occurring Holocene sediments. These are located north and south of the Bohai Sea [52], but not along the northwest coast of the bay. As is usually associated with Cu contents, which may be another reasonable explanation for the equal patterns, but also lacks a uniform distribution around the entire Bohai Rim.

A trigger for the moderately increased values of As, Cu, and V throughout the Bohai Sea could be the Liao and Shuangtaizi Rivers (Figure 1a). In the north, they flow through China’s third-largest oil field, with a multitude of pumping stations. Scattered oil slicks attributable to the oil pumping can be seen along the banks of the Liao River and also floating on its surface, ultimately entering Liaodong Bay (Figure 1b,c). Surprisingly, the readings of the river water samples (44–47) and of the associated seawater sample (48), apart from slightly elevated Cd and Pb values, showed only very low levels of HMs as compared to the values of their neighboring locations. However, it is commonly agreed that As, Cu, and V are included in the natural oil floating into the Bohai Sea. The question remains where the oil ends up, and how and within what timespan it undergoes biochemical degradation. Usually, As is filtered out by sediments on the sea floor, which keeps its levels low. However, oil spills may clog up sediments on the ocean floor, preventing the sediments from bonding with arsenic. Such a shutdown of the natural filtration system could cause arsenic levels in seawater (and eventually in the Bohai Sea) to rise [41].

The values for the Cr, Pb, Zn cluster and the connected subcluster of Cd and Ni were significantly increased for all rivers draining into the Yellow Sea, exceeding the relevant guidelines (Figure 7). This metal combination clearly points to effluents from textile printing, dyeing, and chrome tanning [53], which is consistent with the industries located there (Table S1). However, as industrial companies are sparsely scattered in the vicinity, the strength of pollution seems not to be explicable by their activity only. This northern landscape of the Shandong Peninsula is largely characterized by huge farming areas, primarily growing peanuts, maize, and wheat. As the area is drained by a large number of rivers, we researched published data (Table 7) on the HM contents of pesticides and fertilizers used in the region [54–57]. The data clearly indicated high amounts of

Zn > Pb and moderate values of Cr > As for the pesticides used in this area. Fertilizers deployed in the region showed a relation of Cr > Pb = Zn and additional contents of As. The relatively high Zn contents in the river waters compared to Pb and Cr speak more to farming practices as the source, since Zn accumulates only in small amounts during textile printing and dyeing [53]. Cd and Ni showed a distinct increase in values for the Yangting River and an associated sewer (5, 6), whereby its high Cd concentration was also reflected by the nearby seawater samples 3 and 7. The same is true for the increased Cd and Pb values of the Daliao (49) and Daqing (50) Rivers and the associated measurements of seawater sample 48. Possible polluters could be companies that manufacture batteries in the immediate vicinity of all three rivers (Table S1). The strength of pollution discharged from the rivers along the northern coast of the Shandong Peninsula does not mix with the pollution discharged from rivers into the Bohai Sea, as the current of the Bohai Sea here is directed to the east, out of the bay [18].

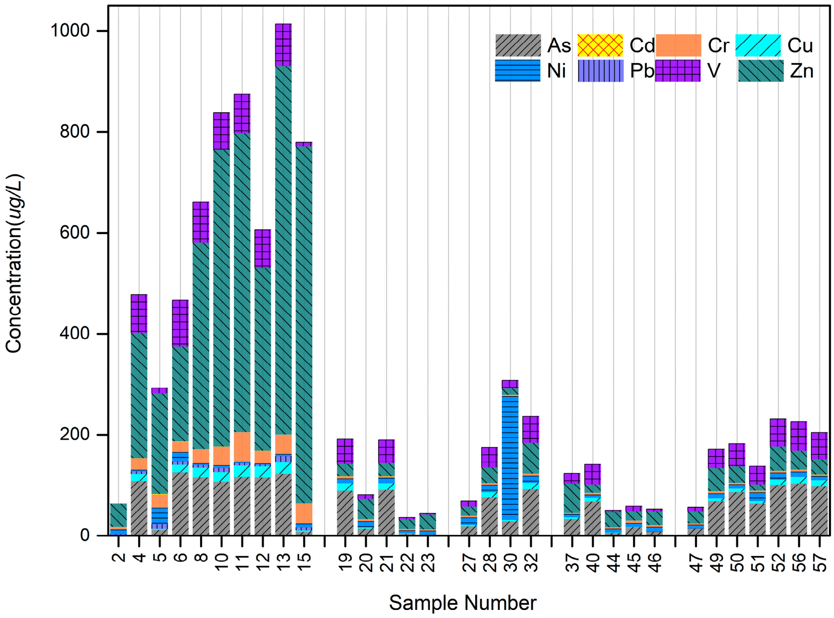

Figure 7. HM concentrations (median values) in the water of all sampled rivers.

Table 7. HM concentrations (mg/kg) in pesticides and fertilizers routinely applied to agricultural land on the Shandong Peninsula.

Chemical Substance		**Zn**	**Pb**	**Cr**	**As**
Pesticides	Herbicide	839.5	250.5	2.2	3.6
	Aphids	753.0	11.6	23.3	6.0
	Urea	3.9	7.5	3.4	0
Fertilizers	Organic	10.08	28.3	38.6	18.5
	Diam.-hydrogen	29.69	15.8	33.2	22.7

Note: Values cited from [54–57].

To determine the degree of pollution and the associated adverse health effects introduced by rivers to each individual bay in the Bohai Sea, HQs were calculated for all HMs in river waters (Figure 8). The results clearly indicated that the HM load of rivers discharging into the Yellow Sea section was significantly higher than in all of the other bays. Cr, Pb, and Zn reached values between 2.5 and 3.5, and even Cd and Cu were at 1.5, indicating that adverse effects are possible and moderate hazards are probable when exposed to the river waters for a longer time. Rivers flowing into the southeast coast of Liaodong Bay were the second most polluted. Rivers draining into Bohai Bay ranked third, followed by those flowing into Laizhou Bay. The lowest values were found for those rivers flowing from the northwest coast into Liaodong Bay. Although the ranking is influenced by the number of rivers per bay and their streamflow (Figures 1 and 8), these results are fully consistent with the findings of other researchers in the past, e.g., with the extent of contamination of the respective coastal sediments in the bay [7].

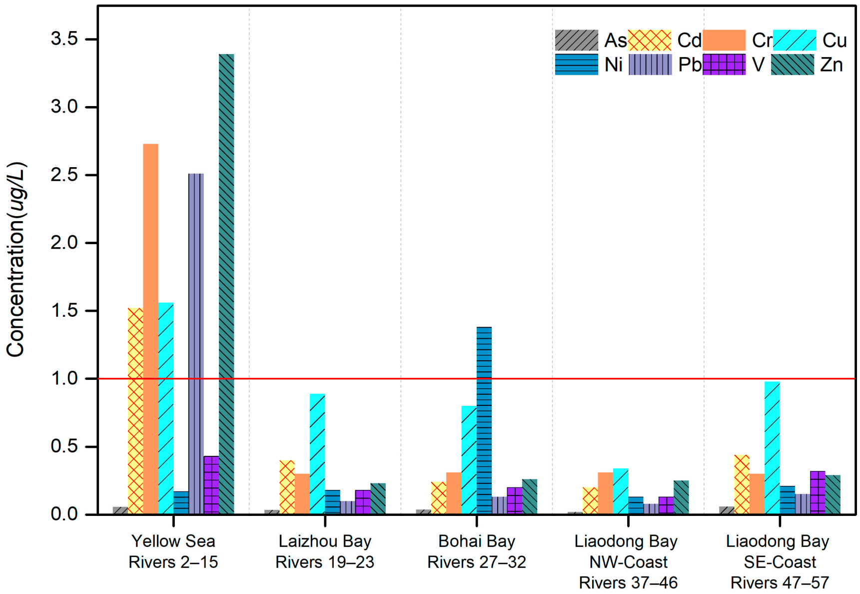

Figure 8. HM hazard quotients of river clusters entering the bays of the Bohai Sea. The references used for calculation were the US-EPA's CCC values [34]. For values greater than one (red line), the exposure concentration exceeds the reference concentration.

6. Conclusions

The investigations carried out in this study focused for the first time on the simultaneous acquisition and consecutive analysis of the HM contents of all major rivers discharging into the Bohai Sea. One goal was to determine whether measures taken in recent years have been successful in reducing the discharge of wastewater into rivers flowing into the Bohai Sea. In this context, it was found that, compared to previous studies, the HM contamination in river waters has decreased for all measured elements, with As and Ni remaining stable. Therefore, the HM values of the river water sediments indicate only low-to-moderate pollution. Where seawater measurements are concerned, Cr and Zn are unchanged, Cd and Pb have substantially lowered, and As and Cu have strongly increased. HMs have also reached the food chain, where sea snails in particular contained excessive values for As, Cu, and Zn. Furthermore, we learned more about the distribution of the HM pollution across the individual bays in the Bohai Sea, and we succeeded in linking characteristic HM element associations with local industrial and agricultural activities.

There are certainly constraints when analyzing HM pollution loads in river waters. One problem is that the results can change abruptly within hours or even minutes if, for example, an industrial company opens its floodgates for wastewater without prior notice for a short period of time only. This is a problem that cannot be solved when sampling flowing waters. Another issue may arise when concentrating on filtered water samples only, as metals are partially insoluble in natural waters. Thus, in future studies, we will additionally analyze the HM concentrations of the suspended particulate matter, although a severe rating for the recommended guideline values is secured, as values are usually provided for dissolved metals. In this context, it needs to be stated that the assessment of pollution is based on given guidelines and so-called standards, which often fluctuate strongly between the relevant authorized institutions in different countries. This study did not focus primarily on the absolute HM concentrations measured but, rather, on specific occurrences and relations of HM contamination between all analyzed river waters discharging into different locations. Therefore, the best way to improve the detection of contamination levels in rivers is to carry out repeated measurements throughout the year. Finding the optimal time (e.g., dry or rainy season) seems to be less of a problem, as the respective element concentrations do not change significantly and the mutual concentration ratios remain largely stable [15]. Considering that rivers contribute 80% of the pollution of the Bohai Sea, the pollutants may come from different sources, such as stormwater [58]. Taking into account the results obtained in this study, regular random sample analyses of river waters may be a promising complement to sediment analysis and for the support of future pollution management in the Bohai Rim in general.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w16070982/s1, Table S1: Coordinates of river sampling points and industries located in the vicinity of the rivers.

Author Contributions: Conceptualization, H.K.; methodology, S.Z.; software, R.K.; validation, C.D.; formal analysis, T.C.; investigation, R.K.; resources, R.K.; data curation, H.Y.; writing—original draft preparation, R.K.; writing—review and editing, H.K.; visualization, L.S.; supervision, H.K.; project administration, H.K.; funding acquisition, C.D. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Data available on request due to restrictions privacy. The data presented in this study are available on request from the corresponding author. The data are not publicly available due to [their containing information that could compromise the privacy of research participants].

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