

Investigation of Copper and Zinc on the Content in Haizhou Bay and in *Platycephalus Indicus*

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Abstract

The contents of heavy metals copper(Cu) and zinc(Zn) in water, sediment, fish skin and flesh of fish in Haizhou Bay were investigated twice in 2017 and 2018. It was found that the contents of Cu and Zn increased year by year. In addition, the contents of Cu and Zn in water and sediment decreased with the increase of offshore distance, indicating that the source of importation was terrestrial, which was consistent with the literature reports. Although Cu and Zn in water belong to class one of seawater, according to Müller's accumulation index, Cu in sediments of some sampling sites has been moderately polluted and Zn has also been slightly polluted. Although the content of Cu and Zn in skin and flesh of *Platycephalus indicus* does not exceed the food standard limit, its higher enrichment coefficient increased with the increase of Cu and Zn concentration in water. If the heavy copper and zinc sources imported into Haizhou Bay are not regulated, it may also cause food safety problems for fish.

Keywords: Haizhou bay; Heavy metal; Copper zinc; *Platycephalus indicus*

Introduction

Haizhou Bay was located in the north of Jiangsu Province, China. Beginning in the north of Rizhao Lanshan Town, Shandong Province, it was located in Foshouzi (35°05'55 N, 119°21'53 E) and extending south to Gaogong Island, Lianyungang City (34°45'25 N, 119°29'45 E). It was a trumpet-shaped open bay bordering the Yellow Sea, with a bay mouth width of 42 km and an area of 876.39 km². It was an important aquaculture and fishing base in Jiangsu Province and one of the eight major fishing grounds in China^[1]. In recent years, with the exploitation of marine resources, the development of coastal cities and industrialization, and the frequent trade between coastal ports, the pollution of the marine environment had become increasingly serious, among which heavy metals were important pollutants with potential dangers. Different from other pollutants, heavy metals were typical inorganic toxic substances. They couldn't be degraded by microorganisms in water. They could only migrate and transform between water, sediment and organisms in different valence states, thus dispersing and enriching. Heavy metals in seawater could be enriched in algae and sediment even if their concentration was very low. They were harmful to human health through the transmission of food chain and had become persistent organic pollutants^[2]. It would have a serious impact on the safety of coastal ecological environment. The available data showed that the content of heavy metals in water phase was small, and the content of heavy metals in sediments was much higher than that in corresponding water phase^[3]. Cu and Zn were the main factors in marine heavy metal pollution. Through the study of Cu and Zn, we could understand the pollution status of the whole

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heavy metal from the side. Therefore, the investigation of Cu and Zn in aquatic and sedimentary was helpful to understand the source and distribution of heavy metal pollution, and also had important environmental warning significance.

Flathead fish (*Platycephalus indicus*) was a kind of off-shore bottom fish, which inhabited shallow sea area. It was usually buried in the sediment of the seabed. It moved slowly and does not form large groups. It was an important fresh-eating fish for coastal residents. Its pollution status had a very direct impact on people's health.

Materials and Methods

Sample collection and processing

In this study, water samples were collected on June 28, 2017 and June 8, 2018, at the peak of the day (shallow silt on the shore, only boat sampling at high tide). Surface water was collected according to the standard of seawater sampling. Sample collection points were shown in Figure. 1 and distributed in Haizhou Bay, totaling 8 points. After sampled, the content of heavy metals was determined by atomic absorption spectrometry in accordance with Ocean Monitoring Code^[1]. The instrument model was Vari-an AA140/240 of the United States.

The methods of sediment collection, pretreatment, preparation, preservation and determination were all in accordance with the requirements of reference^[4]. Surface sediment was collected by grab sampler. Surface 0-2cm mud samples were collected by plastic spoon without disturbance in the center. The samples were described and recorded on site. Number was put into clean polyethylene bag and stored at 0-4°C. Samples thawed to room temperature are air-dried in a cool and ventilated place in the laboratory. Gravel, shells and sawdust are removed. Agate mortar is used to grind them and pass through 160 mesh sieve. Samples were taken after full mixing for determination and analysis.

Flathead fishes were caught in the Haizhou Bay area while sampling. According to the method of literature^[5], the Cu and Zn in fish skin and meat were determined respectively.

Method of evaluating heavy metal pollution level- geoaccumulation index

Geoaccumulation Index (I_{geo}) was a quantitative index for studying heavy metals in sediments proposed by German scientist Müller^[6] in 1969. It could be used to evaluate the pollution degree of heavy metals. The formula is as follows:

$$I_{geo} = \log_2 C_n / 1.5B_n$$

In the formula: C_n was the measured element n content, B_n was the geochemical background value of the element, and the element content that was not polluted is generally selected. The industrialization of Haizhou Bay began gradually after 1990. Therefore, the background values of elements in coastal soils of Jiangsu Province were obtained from 1980 to 1981 in literature^[7], in which $C_{Cu} = 15.02$ ppm and $C_{Zn} = 47.15$ ppm. $I_{geo} < 0$, no pollution; $0 < I_{geo} < 1$, light pollution; $1 < I_{geo} < 2$, moderate pollution; $2 < I_{geo} < 3$, moderate pollution; $3 < I_{geo} < 4$, heavy pollution; $4 < I_{geo} < 5$, heavy pollution; $I_{geo} > 5$, serious pollution.

Bioconcentration factors (BCF)

Bioconcentration coefficient referred to the ratio of the concentration of an element or compound in an organism to that of the substance in the environment in which it lived. It can express the quantitative relationship between the bioaccumulation, concentration, accumulation, amplification and absorption capacity and the degree. The calculation formula was as follows:

$$BCF = C_b / C_w$$

Among them, C_b was the content of heavy metals in organisms; C_w was the content of heavy metals in water.

Results and Discussion

Content of Cu and Zn in Seawater of Haizhou Bay

Figure 1, 2 and 3 showed that the contents of Cu and Zn in sea water in 2018 were higher than those in 2017, which indicated that the contents of heavy metals in sea water in Haizhou Bay were increasing. The closer offshore, the higher the content of heavy metals, which was the same as that, reported in literature^[8]. The reason was that Cu and Zn in seawater came from land input. The relatively high concentration of Cu and Zn in sampling points 3 and 4 was related to the topography of Haizhou Bay. Although sampling point 4 was located in Linhong estuary, there are tidal gates built on Linhong River, which seldom open, so the area actually formed a concave shape. It was possible to accumulate higher concentrations of Cu and Zn due to the concentration of seawater.

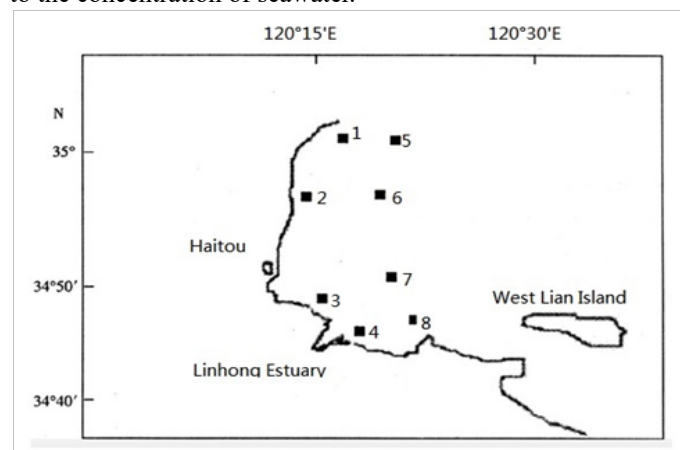


Figure 1: Location of sample sites

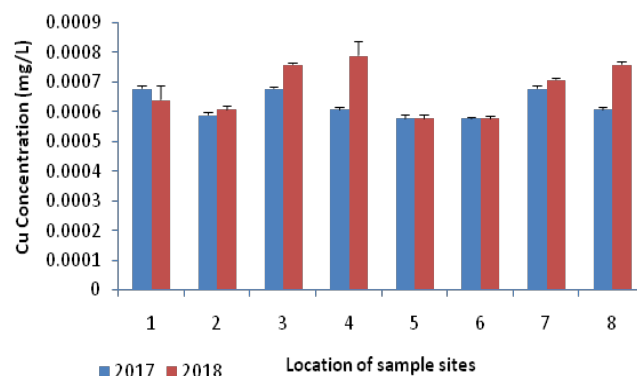


Figure 2: Comparison of Cu concentration in seawater of Haizhou Bay in 2017 and 2018

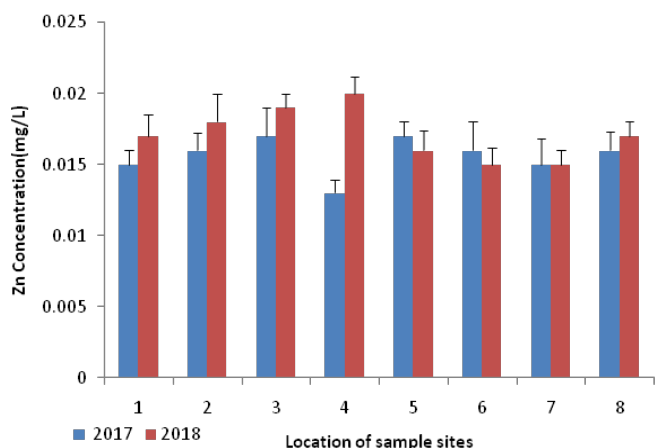


Figure 3: Comparison of Zn concentration in seawater of Haizhou Bay in 2017 and 2018

Pollution assessment of Cu and Zn in water samples and sediments

According to literature 8, it was known that Cu and Zn in Haizhou Bay were the result of land runoff input and coastal deposition. The geo accumulative index of sediment plots at each sampling point in Table 1 showed that the Cu and Zn in the sediments of other sampling points were basically from mild to moderate pollution except sampling point 1. The results of moderate or even heavy pollution at Sampling Point 1 might be related to the ongoing port construction nearby. Referring to the Water Quality Standard of the People’s Republic of China (GB 3097-1997) and the Quality Standard of Marine Sediments of the People’s Republic of China (GB 18668-2002), Cu and Zn in seawater belonged to the first class of water and belonged to cleaner water, while the content of copper in most sampling points of sediments was in the second class of standards, and the content of zinc was in the lower position of the first class of standards. The content of Cu and Zn in sediments was obviously higher than that in water. The results showed that Cu and Zn have high enrichment ability in sediments. Although the slow increase of heavy metals in seawater would not immediately cause a significant decline in seawater quality, it might cause serious pollution of sediments.

Table 1: Cu and Zn geo-accumulation index of different location of sample sites in 2017 & 2018

Item	Location of sample sites							
	1	2	3	4	5	6	7	8
Cu of 2017	2.28	1.38	1.63	1.65	1.38	1.30	0.08	-0.02
Cu of 2018	2.26	1.40	1.65	1.71	1.39	0.29	0.14	0.09
Zn of 2017	0.86	0.84	0.97	0.90	0.90	0.63	1.28	1.54
Zn of 2018	3.22	0.90	1.12	1.29	0.89	0.06	2.35	2.74

Content and Evaluation of Cu and Zn in *Platycephalus indicus*

The results showed that the contents of Cu and Zn in the flesh and skin of *Platycephalus indicus* did not exceed the stipulated values of the National Food Safety Standard (GB2762-2012), but Table 2 could infer that with the increase of Cu and Zn in seawater, the contents of heavy metals in fish meat and skin also

increased correspondingly, so we should be vigilant about the contents of heavy metals in seawater. In addition, the content of Cu and Zn in fish skin was higher than that in fish flesh, which indicated that adsorption had a great influence on the enrichment of organisms. This study was helpful to guide people to pay attention to the hygienic condition of fish skin in their daily diet.

Table 2: Cu and Zn concentration in flesh and skin of *Platycephalus indicus* from Haizhou Bay (mg/Kg)

Heavy metals	Fish skin		Flesh of fish	
	2017	2018	2017	2018
Cu	0.4469 ± 0.0009	0.5571 ± 0.0028	0.3218 ± 0.082	0.3589 ± 0.048
Zn	2.482 ± 0.0166	3.334 ± 0.0167	1.0468 ± 0.2974	1.2968 ± 0.0868

Table 3: Cu and Zn BCF in flesh and skin of *Platycephalus indicus* from Haizhou Bay

Heavy metals	Fish skin		Flesh of fish	
	2017	2018	2017	2018
Cu	714	826	514	532
Zn	159	194	67	76

Bioaccumulation of Cu and Zn in Meat and Skin of *Platycephalus indicus*

According to the calculation of bioaccumulation coefficient of Cu and Zn in the meat and skin of *Platycephalus indicus*, the bioaccumulation ability of copper in *Platycephalus indicus* was much higher than that of zinc. Enrichment coefficient increased with the increase of concentration in water. Biological enlargement effect on environmental pollutants should be noticed by researchers.

Conclusion

1. Similar to the report in literature 8, the source of Cu and Zn in Haizhou Bay might be caused by land importation, and the monitoring of land-based pollution sources should be controlled.
2. Compared with the data of 2017 and 2018, except for the sample points, the content of Cu and Zn was increasing, which indicated that if no further measures are taken, the pollution of heavy metals would be aggravated.
3. The content of Cu and Zn in the body of *Platycephalus indicus* was higher than that in the water sample and sediment, which indicated that the bioaccumulation effect of Cu and Zn in *Platycephalus indicus* was obvious, and the content of Cu and Zn in the skin was higher than that in the flesh, which indicated that the skin adsorption effect was greater than the bioaccumulation effect, and had guiding significance for human dietary habits.
4. Although the content of Cu and Zn in the water did not reach the level of pollution warning, the heavy metals in the sediments of some areas on the surface of the ground accumulated number had reached the level of moderate pollution, and their future harm could not be neglected due to the biological amplification effect.

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