Review Article

The Distributional Characteristics of Heavy Metal in Jiangsu Province Shoal Sea

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After the analysis of surface samples and core samples collected in Xinyanggang tidal land, the contents of Pb, Cu, Zn, and Cr were obtained and analyzed in this paper. The heavy metal accumulation rule and pollution status were studied by Index of geo-accumulation, latent ecological risk index method, and elements accumulation index method. The research suggests that (1) the contents of heavy metal Pb, Cu, Zn, and Cr in Xinyanggang tidal land have the same change trend, and such trend remains unchanged after the data were normalized, while the fluctuation range becomes smaller. (2) After analyzing the heavy metal content in the surface samples, it was revealed that the contents of heavy metals are getting lower from high tidal zone to low tidal zone, but the ranges of the change were different. Cu, Ni, and Zn emerge obvious decline from supratidal zone to subtidal zone, while the changes of Cr and Pb are not obvious. (3) Pb and Cr contents in Xinyanggang tidal land present accumulative character, as Pb in Xinyanggang is 3 times as much as the local background value, whose EF reaches 3.774. (4) RI value in Xinyanggang is 23.552, which indicates that though Xinyanggang tidal land has some heavy metal pollution and accumulation, there are no ecosystem risks, and the whole Xinyanggang core area environment quality is relatively good.

1. Introduction

As a special coastal wetland, tidal wetland is a complicated multiple-functional ecosystem with unique ecovalue and resource potential. In tidal zone, heavy metals cannot be purified through water self-purification; they normally sink into sediments after deposition and accumulation in tidal land through complicated physical, chemical, and biological process. Xu carried out researches on the spatial distributions of heavy metals and their dynamic accumulating characteristics in Shanghai coastal tidal land [1] which indicate that, in large scale, the spatial distribution pattern of the heavy metal Cu, Zn, Cr, and Pb in tidal flat sediments was not directly affected by coastal pollution discharges, rather they were closely related to sediment dynamics; while in small scale, the content of heavy metals in the tidal land near the drain was closely related to the drain. Bi Ch [2] studied different variation patterns of the existing form of heavy metal Cu, Zn, Cr, and Pb in different seasons, different locations in tidal land near the Bailonggang drain, and the shape, content, and distribution in the root sediments, finding that the contents of heavy metals in the tidal land near the Bailonggang drain were all obviously above the background value in the Shanghai tidal flat and that the sewage input had some impact on the existing form of heavy metals in sediments.

Northern-Jiangsu tidal wetland, which is a typical muddy tidal flat wetland, has the greatest area, the maximum ecosystem types, and the most complicated erosion-accumulation changes in China, even in the world. It was formed by the sediments from the ancient Yellow River Delta and Changjiang River Delta, which were washed by wave collisions and tides in the Yellow Sea and the East China Sea. With the length of 444 km, Jiangsu coastal wetland has the area of 5,100 km². Within this area, there are abundant river and marsh developed. The ecosystem in the core area of
Yancheng Reserve remains in natural status, with limited human impacts. Therefore through analysis of tidal flat surface samples and core samples in the core area of the Reserve and the contents of heavy metal Cu, Zn, Cr, and Pb in different geomorphologies and different vegetation conditions and upon verifying between indicators, the following works had been done, that the distribution pattern of the above indicators was discussed, the biogeochemical process in different vegetations and sediments was analyzed, and the roles of different tidal flat geomorphologies and their vegetations in the enrichment of the heavy metals in the whole tidal wetland were compared.

2. Materials and Methods

2.1. The Collection of Samples and Disposal. Between August 17 and 19 2005, two cores (SY01, SY02) were collected in the core area of Yancheng red-crown crane National Natural Reserve (Xinyanggang in Sheyang County); surface samples were collected every 20 m along the cross-section from the west to the east, 220 samples in all, the sampling locations refer to Figure 1. Two cores were collected using 70 mm inner diameter and 75 mm outer diameter PVC pipes which directly access into the ground. It was pointed by the hand GPS, precision 10 m. After sealing at field, we brought them to the lab, took out the samples, dissected, took photos, and described the lithologic characters and deposition configurations. We conserved one-half of the dissected core samples and the other half was divided every 2 cm, 72 parts in total, using freeze-drying machine ALPHA-1-4 produced by the German Martin Christ Company to hypothermia lyophilize samples. For the computation method of water content and volume, refer to Ren M E, 1983. The grain size of the samples was analyzed using the Laser Particle Size Analyzer Mastersizer 2000 produced by Britain, accomplished in the Ministry of Education Key Laboratory For Coast and Islands Development, Nanjing University. The grain size parameters computation used the Moment method.

We took 260 lyophilized samples (including all the surface samples, core samples choosing 0–50 cm, and 50–100 cm every other sample), removed plant debris and stones, ground and passed then through 100 mesh sieve, preserved then in plastic bottles, and then kept then in dryer in order to determine the content of heavy metals. The heavy metal tests were carried out in ICP-MS Heavy Metal Analysis Room of the State Key Laboratory for Mineral Deposits Research, Nanjing University. The process is as follows: weigh 0.5 g sample accurately, then resolve it using HNO$_3$–HCL–HClO$_4$ acid in the triangular flask, slake it in the 2040 programmable slacker, and determine the volume, and determine the content of Cu, Zn, Pb, Ni, Fe, Cr, Fe, Li, Al, and other heavy metals in soil using ICP-MS.

The instruments used are the following: Orient MDS-9000 Microwave Slaking System (Xi’an Aoruite Technology Development Corporation); HP4500series300 Plasma Mass Spectrometer (Hewlett-Packard); Ultra-pure Water NG (MLLI-Q) manufactured by American MLLipore Company. All containers were soaked overnight using 20% hydrogen nitrate and rinsed with water three times.

2.2. Data Handling and Methods. The map of sampling locations and a part of figures and tables were made using Mapinfo 7.0 and Corel draw 10; most figures and data statistical analysis were accomplished using excel 2000 and Origin 6.0, and part of the data was handled and statistically analyzed with SPSS10. and with SPSS10. The correlation analysis between heavy metals and the correlation analysis between heavy metals and grain size were also carried out.

2.3. The Heavy Metal Pollution Evaluation Method

2.3.1. Index of Geoaccumulation. In order to evaluate the enrichment conditions and pollution conditions of heavy metals in the core area, the Index of geoaccumulation, $I_{geo}$, presented by German scientist, Muller, was adopted [3], which was used to quantitatively analyze heavy metal pollution in fluids. Its equation can be seen as follows:

$$I_{geo} = \log_2 \left( \frac{C_n}{A_n B_n} \right).$$

In the above equation, $C_n$ is the content of the $n$ element in the sediment, $B_n$ is the geochemical background value of the bedrock, and $A$ is the constant for modifying the fluctuation of the background value caused by lithogenous movement, usually 1.5. According to this method, the heavy metal pollution in the sediments was divided into 7 degrees, as can be seen in Table 1.
Using the $K_{2.3.3.}$ Sediment Enrichment Factor Method of Heavy Metals. In this paper, the Latent ecological index method put forward by the Sweden scientist Hakanson was adopted [4], which is a method for assessing heavy metals in soils or in the sediments from the perspective of sedimentation based on the nature and the environmental behavior characteristics of heavy metal. This method not only considers the heavy metal content in soils, but also links the ecological effects of heavy metals, environmental effects, and toxicological effects together and adopts the comparable, equivalent attribute index classification method for evaluation. Potential ecological index correlates to the individual pollution coefficient, heavy metal toxicity coefficient, and potential ecological risk individual coefficient; its equation can be seen as follows:

$$E_F = \frac{M_0/L_i}{M_B/L_i}$$

In the above equation, $E_F$ is the heavy metal enrichment factor in sediments, $M_0$ relates to heavy metals content in the tidal flat surface, $M_B$ is the background value of the heavy metal, and $L_i$ means enrichment factor. $L_i$ means the content of Li in the tidal flat sediments, and $L_i$ means the background value of Li. The enrichment factor classification standard can be shown in Table 3.

### 3. Results and Discussions

#### 3.1. The Vertical Variation Pattern of Heavy Metals

After the study on the particle size and the vertical variation pattern of the heavy metals of the core ZXY01, ZXY02, it could be found that (1) the tendency of heavy metal Zn, Pb, and Cu in ZXY01 was basically the same; on the whole it decreased fluctuatingly from the surface to the downward, at $-15$ cm, $-30$ cm, and $-55$ cm, it formed the peak value, while at $-25$ cm, $-55$ cm it formed the valley value; (Pb was noticeably increasing only bellow $-60$ cm, different from the other two metals); the peak and valley values of them were in good coordination. The contents of Fe, Ca, and Mn were fluctuatingly increasing; at $-25$ cm and $-55$ cm it formed the peak value, so they were synchronous (refer to Figure 3). Ni, Cr, and Mg had no obvious increasing tendency; they fluctuated in a certain scope but formed peak value at $-25$ cm and $-55$ cm all the same. (2) After using Li as the standard normalized...
Table 3: Enrichment degree of heavy metals.

| EF     | <0.25 | 0.25~0.5 | 0.5~0.75 | 0.75~1.5 | 1.5~2 | 2~4 | >4 |
|--------|-------|----------|----------|----------|-------|-----|----|
| Enrichment degree | Extremely depletion | Strong depletion | Weak depletion | Proximity enrichment | Weak enrichment | Strong enrichment | Extremely enrichment |

| The average particle size | Sorting coefficient | Skewness | Peakedness | Component (%) | The average particle size | Sorting coefficient | Skewness | Peakedness | Component (%) |
|---------------------------|---------------------|---------|-----------|---------------|---------------------------|---------------------|---------|-----------|---------------|
| 4.5                       | 5.5                 | 6.5     | 7.5       | 8.5           | 9.5                       | 10.5                | 11.5    | 12.5      | 13.5          |
| 4.5                       | 5.5                 | 6.5     | 7.5       | 8.5           | 9.5                       | 10.5                | 11.5    | 12.5      | 13.5          |

Figure 2: Grain size character diagram of cores ZXY01 and ZXY02 in the Xinyanggang tidal flat.

When comparing grain size of ZXY01 with ZXY02, the content of clay and sand of ZXY01 was more than that of ZXY02, and the change from top to bottom was greater. The silt content of ZXY02 was higher than that of the other, while the content of clay and sand from the top to the bottom was relatively stable (Figure 2). Compared with the most heavy metal deposition pattern in North Jiangsu, the heavy metal deposition was mainly controlled by clay content and material source in the sediment and was positively correlated with clay content. This was the reason why the content of Cu and Zn of ZXY02 was less than that of ZXY01 and the changes were more stable (Figure 3). Only the Pb content change had unique accumulating law, and it could be deduced that human activity contributed a great deal to the accumulation of Pb in this area.

3.2. The Horizontal Distribution Pattern of Heavy Metals.

The heavy metal content distribution characteristics of the horizontal section show the decrement trend from high tide zone to low tide zone, but the decrement speed varied. As observed the content of Cu, Ni, and Zn declined more notably from the upsurge to the low ebb, while Cr, Pb had no obvious decreasing trend, showing that the content of Cr, Pb in tidal flat sediments was not significantly affected by water dynamic. Particularly Pb gas deposits accounted for larger proportion. Seeing from fluctuation amplitude, Zn, Pb had larger fluctuation amplitude, respectively, 79.19~63.92 (μg/g) and 71.54~58.7 (μg/g), and the other elements had
smaller fluctuation amplitude, copper: 29.98–24.07 (µg/g), Ni: 25.08–19.52 (µg/g), and Cr: 58.31–48.79 (µg/g). As can be seen from Table 4, the content change scope of surface heavy metals of Xingyanggang core area was smaller than that of Sheyang County in comparison, so it could be seen that overall protective effect was better in the core area.

4. Heavy Metal Pollution Evaluation

4.1. The Present Heavy Metal Pollution Analysis. After analyzing 220 surface samples, in general, the content of the chemical elements of Xingyanggang tidal wetlands was in the following order: Mn> Pb> Zn> V> Cr> Cu> Li> Ni. In this paper, representative elements Cu, Pb, Zn, and Cr were used to evaluate tidal flat heavy metal pollution as indicators, which could indicate the human activity impacts on the tidal flats. Many researchers use the average value of shale presented by Turekian and Wedepohl [7] or the average crustal abundance value presented by Taylor [8] as a reference background value. However, in different regions due to different sediment sources, background values should be chosen which had comparable mineral compositions with contaminated sediments and had unpolluted sediment elements value, namely, from the deepest core sites with the absence of bioturbation, so the trace elements prior to the industrialization activities were estimated to be background values [5]. Xingyanggang region was a traditional agricultural area, the core area protected well, and no large-scale development conducted, basically in pristine natural state. Throughout

| Element | Cu (µg/g) | Cu/Li | Fe (%) | Fe/Li | Mg (%) |
|---------|-----------|-------|--------|-------|--------|
| 0       | 20        | 24    | 28     | 60    | 2.2    |
| 20      | 0         | 20    | 20     | 60    | 2.2    |
| 40      | 0         | 20    | 20     | 60    | 2.2    |

| Element | Zn (µg/g) | Zn/Li | Pb (µg/g) | Pb/Li | Ni (µg/g) |
|---------|-----------|-------|-----------|-------|-----------|
| 60      | 60        | 60    | 60        | 60    | 60        |
| 80      | 80        | 80    | 80        | 80    | 80        |
| 100     | 100       | 100   | 100       | 100   | 100       |

**Figure 3:** Metal content change map of Xinyanggang pillars ZXY01 and ZXY01.
Table 4: Heavy metal content of surface samples in Xingyanggang tidal flat.

| Elements | Surface samples of Sheyang County | Surface samples in Xingyanggang tidal flat |
|----------|-----------------------------------|--------------------------------------------|
|          | Mean value                        | Variation scope                            | Mean value                        | Variation scope                            |
| Zn       | 72.2                              | 79.19–63.92                               | 68.95                              | 73.14–64.02                               |
| Pb       | 65.76                             | 71.54–58.7                                | 65.83                              | 71.88–56.01                               |
| Co       | 14.28                             | 15.37–12.99                               | 14.27                              | 15.53–13.09                               |
| Ni       | 22.96                             | 25.08–19.52                               | 22.52                              | 23.85–21.3                                |
| Mn       | 481                               | 506.6–449.7                               | 443.98                             | 477.1–397.8                               |
| Cr       | 53.6                              | 58.31–48.79                               | 52.83                              | 56.28–48.42                               |
| Cu       | 27.77                             | 29.98–24.07                               | 20.84                              | 22.87–18.14                               |
| Li       | 32.8                              | 36.39–28.87                               | 31.49                              | 33.78–30.05                               |

Table 5: Heavy metal content and background values in Xinyanggang tidal land.

| Area                                      | Pb (µg/g) | Zn (µg/g) | Cu (µg/g) | Cr (µg/g) | Li |
|-------------------------------------------|-----------|-----------|-----------|-----------|----|
| Background value in Xinyanggang tidal flat | 21.05     | 88.5      | 21.35     | 46.8      | 38 |
| Mean value in Xinyanggang tidal flat      | 65.83     | 68.95     | 20.84     | 52.83     | 31.49 |
| Maximum value in Xinyanggang tidal flat   | 71.88     | 73.14     | 22.87     | 56.28     | 33.78 |
| Minimum value in Xinyanggang tidal flat   | 56        | 64.02     | 18.14     | 48.42     | 30.05 |
| Background value in north shore tidal flat of Changjiang estuary | 22.11 | 112 | 15 | 60 | 38 |
| Background value in eastern China tidal flat | 20 | 65 | 15 | 60 | 38 |
| Marine survey value in Jiangsu tidal flat heavy metal survey in 1986 | 25 | 80 | 30 | 45.7 |
| Marine baseline survey value of Dafeng County in 1997 | 28.06 | — | — | — |

From \( I_{geo} \) value, Xinyanggang Pb pollution reaches partial pollution degree, while Zn, Cr, Cu, and Li are not polluting, corresponding to the former research results in the preamble.

4.2. The Vertical Change of Heavy Metal Pollution. According to \(^{210}\)Pb dating method, the average sedimentary rate of Xinyanggang tidal flat was 2.85/a, so that heavy metal pollution change process in the last 25 years can be obtained from the study of core samples (Figure 4). It is showed by ZXY01...
Table 6: Estimation result of the ecological damage of heavy metals from Xinyanggang tidal flat.

|                | Tide beach | In the tidal flat | The ebb shoal |
|----------------|------------|-------------------|---------------|
| $C_{Pb}$       | 3.127      | 3.055             | 3.190         |
| $C_{Cu}$       | 2.108      | 1.842             | 1.198         |
| $C_{Zn}$       | 1.339      | 2.069             | 1.006         |
| $E_{Pb}$       | 15.635     | 22.7775           | 20.950        |
| $E_{Cu}$       | 15.540     | 11.210            | 5.990         |
| $E_{Zn}$       | 6.439      | 6.052             | 2.017         |
| RI             | 23.552     | 36.0835           | 27.946        |

The evaluation results: Slight ecological risk, Slight ecological risk, Slight ecological risk.

Figure 4: Vertical change process of heavy metal pollution in Xingyanggang tidal flat.

and ZXY02 that since 2001, $I_{geo}$ value of Pb in Xinyanggang is above 1, indicating middle plus level pollution. From 1974 to 1981, Pb pollution was on the downward trend, which was because lead content in fuel was controlled by law. From 1981 to 1997, Pb pollution fluctuated in the low level; after 1997, Pb pollution was on an upward trend, which was related to the development of Sheyang chemical and metallurgical industries, and so forth [10]. Thus, it was proposed that a buffer zone should be set up between the core area and the development zone to better protect the core area environment. The research showed that no significant Cu, Zn pollution occurred in the tidal flat of Xinyanggang core zone, and Cu, Zn pollution was on the downward trend. Although there was minor contamination of Cr (–1–0.2), it was only a lighter extent and on a downward trend. This showed that since the nature Reserve establishment in the core area in recent years, good effects have achieved.

4.3. The Potential Ecological Harm Analysis of Heavy Metals. Upon study, it was found that there were a certain enrichment and pollution of heavy metal Pb, Cr in Xinyanggang core area. In order to find out the heavy metal impact in the core area on the national protection animal, the red-crowned crane, and on the ecological environment pollution, the potential ecological index method was adopted which was presented by Swedish scientist Hakanson, which is a method for assessing heavy metals in soils or in the sediments from the perspective of sedimentation based on the heavy metal nature and its environmental behavior characteristics. This method not only considers the content of heavy metals in soil, but also links the ecological effects of heavy metals, environmental effects and toxicological effects together. The results showed that (see Table 6) Pb, Zn, Cu, and Cr had no ecological pollution, Pb had the highest indexes, and its $E_{Pb}^i$ and $C_{Pb}^f$ reached 15.635 and 3.127, both in the minor scope of ecological harm. The indicators' order from high to low was Pb, Cr, Cu, and Zn, all in a safe area, and ecological pollution hazards had not appeared yet. RI value was 23.552, far less than light ecological hazard upper limit 150, indicating that although there were some heavy metal enrichment and pollution in the core area, yet no ecological hazards had been produced, and overall environment quality in Xinyanggang core area was excellent.

5. Conclusions

Through research it could be found that (1) the contents of heavy metal Pb, Cu, Zn, and Cr in Xinyanggang tidal
land have the same change trend, and the fluctuation range becomes greater from deep part to surface. After using Li as the standard normalized element, the fluctuation ranges of all heavy metal normalized elements were significantly narrower than that of the heavy metals' content, with the former peaks and troughs lagging behind the latter. The main fluctuation trend keeps unchanged. The change trend of Pb/Li was counter to that of Pb content. (2) From the heavy metal content distribution characteristics of the horizontal section, we can find that they all displayed the decreasing trend from high tide to low tide, but the decreasing speed varied. The contents of Cu, Ni, and Zn declined more notably from the upsurge to the low ebb, while Cr, Pb had no obvious decreasing trend. (3) Cr and Pb in Xinyanggang tidal flat showed different enrichment degree, in which Pb exceeded the standard most, with EF value reaching 3.774, three times as much as the background values of China east coast. Its enrichment degree in Xinyanggang tidal flat reaches the strong enrichment scope, so Pb pollution is significant. (4) Xinyanggang RI value is 23.552, far less than light ecological hazard upper limit 150, indicating that although there are some heavy metal enrichment and pollution in the core area, no ecological hazard has been produced yet, and overall environment quality in Xinyanggang core area was excellent.

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