# Characteristics of Heavy Metal Enrichment of Vegetation Rhizosphere Sediment in Intertidal Salt Marsh of Minjiang River Estuary

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Abstract: In order to investigate the characteristics of heavy metal elements enrichment in the rhizosphere sediments of different vegetation types, several cores of the rhizosphere sediments (0~20 cm) were collected from different vegetation types zone in intertidal wetland of Langqi Island, the Minjiang estuary. The results demonstrate that heavy metals have obvious enrichment at the depth of 2 cm in the sediment surface in the rhizosphere of Spartina alterniflora, Scirpus mariqueter and Phragmites australis. Heavy metals also showed obvious accumulation at the depth of 10~12 cm in the rhizosphere sediments of Scirpus mariqueter and Phragmites australis, while Spartina alterniflora did not show this feature. The content of heavy metals in the rhizosphere sediments of Scirpus mariqueter reached its lowest value at the depth of 16 cm, then increased with depth. It is speculated that the adsorption of heavy metals by the roots of Scirpus mariqueter mainly concentrates at the depth of 16 cm. Pearson correlation analysis was conducted on the changes of heavy metal in sediments under different vegetation, shows that obvious positive correlation is observed between Cu, Fe, Mn, Pb and Zn, indicating that they have similar sources and may have a certain relationship with human activities. However, Cr, Sr is more likely to come from natural sources. The enrichment of Rb, Zr may be influenced by the selective adsorption of different plant roots or other environmental factors.

## 1 INTRODUCTION

The coastline of China is long and has developed a broad muddy coast (tidal flats). The tidal flats are affected by many factors such as cyclical tide and vegetation growth, which cause significant changes in redox conditions, organic matter degradation, and microbial activity (Wang et al., 2012). Changes in these factors have an important impact on the accumulation, change and migration of heavy metals in sediments. The estuary tidal flats are affected by the two-way currents of rivers and seas. They have complex hydrodynamic actions and frequent changes in erosion and siltation. They are typical environmental fragile zones and sensitive zones and are highly susceptible to sudden events such as severe weather and storm surges (Yu et al., 2009). When the sediment is disturbed, heavy metal elements will be released into the environment and cause secondary pollution (Wang et al., 2005). Tidal flats sediments as potential sources of heavy metals may contaminate the surrounding aquatic ecosystem and may be toxic to aquatic organisms (Wang et al., 2012). More importantly, heavy metals can be absorbed by aquatic organisms, and thus enter the food chain, transfer to the superior nutrition layer, and become a potential source of toxicity to humans (Ke and Wang, 2012). Therefore, the accumulation and cycling of heavy metals have been a concern for tidal flats in estuarine ecosystems (Reboreda and Caçador, 2007; Duarte et al., 2010; Koretsky et al.,2007).

The Minjiang River estuary is a strong tide estuary that develops submarine deltas and forms a broad muddy coast. In recent decades, the exotic species *Spartina alterniflora* has rapidly spread and



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is bound to affect the tidal flat wetland ecosystem of the Minjiang River estuary. At present, there are few reports on the characteristics of the heavy metal accumulation in the tidal flat wetland of the Minjiang River estuary and its relationship with environmental factors. In this paper, the characteristics of heavy metal accumulation in the rhizosphere sediments of different vegetation types in the Minjiang River estuary are studied. It will not only contribute to the development of resources and environmental remediation in the Minjiang River estuary, but also provide scientific theoretical basis for the conservation, maintenance and restoration of the tidal flat wetland ecosystem in the Minjiang River estuary.

# 2 MINJIANG RIVER ESTUARY TIDAL FLAT WETLAND OVERVIEW

The Minjiang River is the largest river in Fujian province and originated in Wuyi Mountain in western Fujian. The basin area is 60,992 km$^2$, accounting for about one-half of the total area of Fujian Province. The Minjiang River estuary is an important material distribution center, and it is also the seat of Fuzhou city, the provincial capital of Fujian and plays an important role in the economic development of Fujian Province. The Minjiang River estuary is a strong tide estuary that develops submarine deltas and forms a vast muddy coast. The tidal flat wetland is affected by the regular half-day tide, and the tidal creek system develops, forming a typical tidal flat salt marsh. From land to sea, it can be divided into high tidal flats, medium tidal flats and low tidal flats. The tidal flat vegetation is dominated by *Phragmites australis*, *Spartina alterniflora* and *Scirpus mariqueter*. *Phragmites australis* mainly grow on high tidal flats. *Spartina alterniflora* and *Scirpus mariqueter* grow on medium tidal flats. The vegetation growth density gradually decreases from high tidal flats to low tidal flats. *Phragmites australis* and *Scirpus mariqueter* are the primary vegetation in this area, and *Scirpus mariqueter* is a unique salt herb in China. *Spartina alterniflora* is a perennial salt marsh plant native to the Atlantic coast of the United States, and it has superior reproduction and diffusion capabilities. Since it was introduced in 1979, it has rapidly spread in coastal areas of China. At present, from the north of Liaoning province to the south of Guangdong province, the invasion area of *Spartina alterniflora* has reached 56,000 hectares, which poses a serious threat to the conservation of biodiversity and ecological security in tidal flats.

# 3 SAMPLE COLLECTION AND EXPERIMENTAL METHODS

## 3.1 Sample Collection

In October 2015, six columnar samples of plant rhizosphere sediments were collected from a typical vegetation zone in the Dongtan of Langqi island using a PVC pipe about 8 cm in diameter (Figure 1). The length of the column sample was 20-25 cm, and 2 of them were located in a typical *Phragmites australis* growing area, 2 of them are located in the *Spartina alterniflora* growing area, 2 of them are located in the *Scirpus mariqueter* growing area, but the latter has a sporadic distribution of *Spartina alterniflora*. The samples were packaged in polyethylene bags and placed vertically and returned to the laboratory for separation. The columnar samples were divided according to 0~1 cm, 1~2 cm, 2~4 cm, 4~6 cm, 6~8 cm, 8~10 cm, 10~12 cm, 12~14 cm, 14~16 cm, 16~18 cm and 18~20 cm.

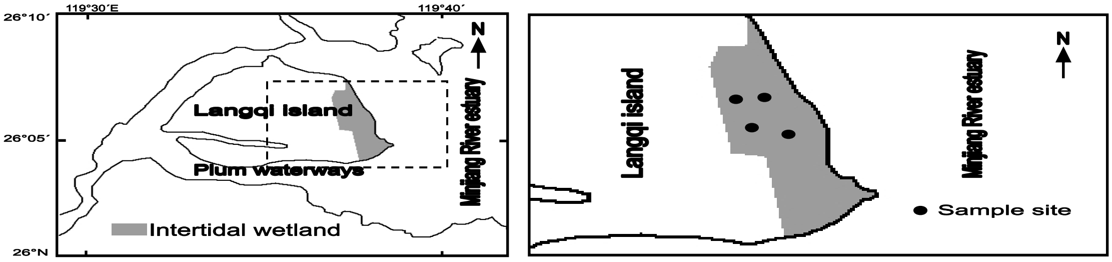


Figure 1: Location map of the study area and sampling sites.

### 3.2 Experimental Methods

In this study, the contents of Cu, Fe, Mn, Ni, Pb, Zn, Rb, Sr, Zr, Cr in the rhizosphere sediments of the tidal flat vegetation in the Minjiang River estuary were tested and analyzed. The heavy metal of the sample was measured using XRF-1800 scanning X-ray fluorescence spectrometer. The sample was dried in an oven at 40°C for 72 hours and then fully ground using an agate mortar. After sifting through a 100-mesh sieve, 2~4 g of the sample were placed in a polyethylene disk and samples with an inside diameter of approximately 30 mm and an outside diameter of approximately 40 mm are produced at pressure of 37.5 t. This method selected standard water system deposition materials (GSD-9, China Stream Sediment Reference Material) as the control standard (Wu et al., 2015).

## 4 CHARACTERISTICS OF HEAVY METAL ACCUMULATION IN RHIZOSPHERE SEDIMENTS OF TIDAL FLAT VEGETATION

### 4.1 Enrichment Characteristics of Heavy Metals in Rhizosphere Sediments of Phragmites Australis

The vertical variation of heavy metal in the rhizosphere sediments of *Phragmites australis* is obvious (Figure 2). Cu, Fe, Mn, Ni, Pb, Zn, Sr, Zr and Cr are significantly enriched at the depth of 2 cm, after that, the content of heavy metal decreases with depth. However, the enrichment of Rb at the depth of 2 cm is not significant. All of the 10 elements were significantly enriched at 10-12 cm, and at the depth of 6 cm, there are low content. Below 12 cm, the contents of Cu, Fe, Mn, Ni, Pb, Zn, Rb, Sr, and Cr decreased significantly with depth. However, the Zr does not decrease with depth below 12 cm. Rb and Sr are enriched at the depth of 16 cm, and Fe, Mn, Ni, Zn and Cr also reflects this feature but not significant. With the exception of Cr, the enrichment of the other 9 elements at the depths of 10-12 cm was significantly stronger than that at the depths of 2 cm.

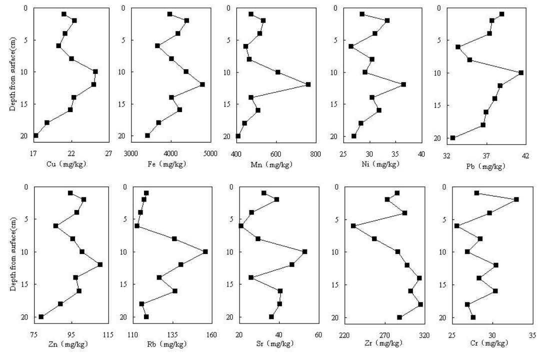

Figure 2: Distribution profiles of heavy metal concentrations in the rhizospheric sediments of *Phragmites australis.*

### 4.2 Enrichment Characteristics of Heavy Metals in Rhizosphere Sediments of Scirpus Mariqueter

The vertical variation of heavy metal elements in the rhizosphere sediments of *Scirpus mariqueter* was similar to that of *Phragmites australis* at 0-12 cm depth (Figure 3). At the depths of 2 cm and 12 cm in the sediments, there was significant heavy metal enrichment. Below 12 cm, the content of heavy metal decreases with depth. However, below 16 cm, the contents of Cu, Fe, Mn, Ni, Pb, Zn, Rb, Sr and Zr showed a gradually increasing with depth. The content of Cr reached the lowest value at the depth of 6 cm, and then it increased significantly with depth, reached the highest value at the depth of 14 cm. Afterwards, it showed a decreasing trend until it reached the depth of 18 cm, and then it showed a tendency to increase with depth.

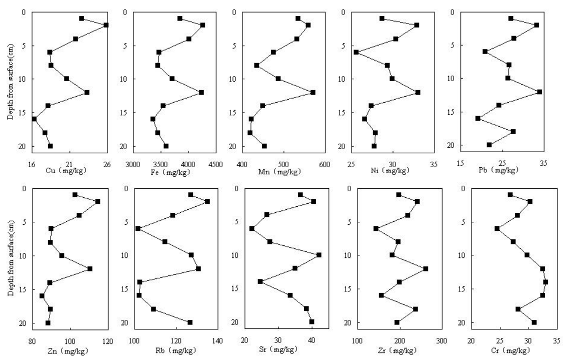

Figure 3: Distribution profiles of heavy metal concentrations in the rhizospheric sediments of *Scirpus mariqueter.*

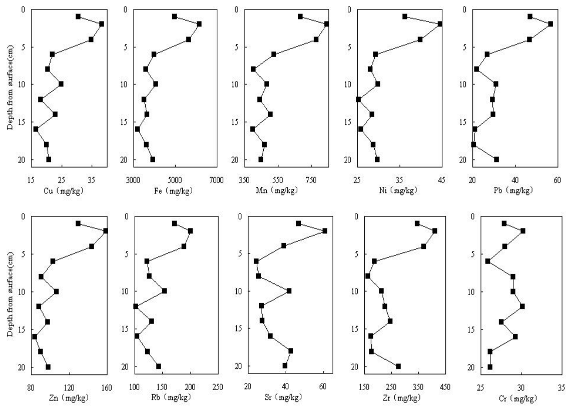


Figure 4: Distribution profiles of heavy metal concentrations in the rhizospheric sediments of *Spartina alterniflora.*

### 4.3 Enrichment Characteristics of Heavy Metals in Rhizosphere Sediments of Spartina Alterniflora

The vertical variation of heavy metal in the rhizosphere sediments of *Spartina alterniflora* was significantly different from that of *Phragmites australis* and *Scirpus mariqueter*. The heavy metal were significantly enriched at the depth of 2 cm, and then decreased with depth (Figure 4).

## 5 RESULTS AND DISCUSSION

### 5.1 Key Features of Enrichment of Heavy Metals in Rhizosphere Sediments of Tidal Flat Vegetation

The vertical variations of heavy metal in the rhizosphere sediments of different vegetations in the tidal flats are similar, and they are significantly enriched at the depth of 2 cm. It is more obvious in *Spartina alterniflora* and *Scirpus mariqueter*. The heavy metal accumulation in the rhizosphere sediments of *Phragmites australis* and *Scirpus mariqueter* was significant at the depth of 10~12 cm, while *Spartina alterniflora* did not show this feature. At the depth of 12 cm, the heavy metal decreased significantly with depth. This change is also reflected in previous studies. For example, in the study of tidal flat sediments on the south bank of Tivoli in New York, the three heavy metal elements were significantly enriched at the depths of 13~15 cm. At the depth of 18~20 cm, the content of heavy metal decreases rapidly with depth, reaching the background value at about 50 cm (Gaboury et al., 1999; Wang et al., 2002).

The rhizosphere of plants has an important adsorption effect on heavy metal elements. During the plant growing season, heavy metal in sediments of the tidal flats was significantly reduced. Relative to plant leaves and stems, plant roots have the highest concentrations of heavy metals (Wang et al., 2002). The content of heavy metals in the rhizosphere sediments of the three plants of the Minjiang River estuary were significantly enriched at the depth of 2 cm, which may be due to the fact that heavy metals in surface sediments are less affected by the absorption of plant roots. The roots of *Scirpus mariqueter* are concentrated below the depth of 10 cm (Wang et al., 2012), and the heavy metals in the surface sediments are less affected by the absorption of plant roots, resulting in higher heavy metal content at the depths of 2 cm and 10~12 cm, and a minimum of heavy metal content at depths of 16 cm. Later, as the depth increases, it shows a gradual increase. It can be inferred that the adsorption of heavy metals by the roots of *Scirpus mariqueter* is mainly concentrated at the depth of 16 cm. The roots of *Phragmites australis* are mainly concentrated at 20~80 cm below the surface (Wang et al., 2012). It has less adsorption of heavy metals on surface sediments, which may lead to more obvious enrichment of heavy metals at 10~12 cm than that of *Scirpus mariqueter*. From 12 to 20 cm, heavy metal gradually decreased with depth, indicating that the adsorption of heavy metals by the roots of *Phragmites australis* gradually increased. The contents of heavy metals in the rhizosphere sediments of *Phragmites australis* and *Scirpus mariqueter* have a significant low value at the depth of 6 cm. This phenomenon is not caused by the adsorption of plant roots. The specific mechanism needs further research. Roots of *Spartina alternifolia* are more developed and a longer growing period than *Phragmites australis* and *Scirpus mariqueter* (Li et al., 2009). Its adsorption capacity for heavy metals is also stronger. This feature may lead to significant adsorption of *Spartina alterniflora* to heavy metals in sediments at the depths of 10~12 cm. As a result, *Spartina alterniflora* did not show similar characteristics of heavy metal enrichment to those of *Phragmites australis* and *Scirpus mariqueter*.

## 5.2 Correlation Analysis

Pearson correlation analysis was conducted on the heavy metal of different vegetation rhizosphere sediments (Table 1, Table 2, Table 3). The results showed that Cu, Fe, Mn, Pb, and Zn were strongly correlated in the rhizosphere sediments of the three plants, it can be speculated that these five elements have similar sources. There is no obvious correlation between Cr, Sr and other elements, and Cr, Sr are more likely to come from natural sources, such as atmospheric deposition, changes in geochemical composition, etc. The results of this study are in good agreement with previous studies. Studies on the surface sediments of Shanghai no residential island have also confirmed that the sources of Cu, Pb, and Zn are related to the effects of human activities, and Cr is more likely to come from natural source (Yang et al., 2011). Ni is an iron-friendly elements that may be affected by changes in Fe. Rb and Zr have no good correlation with other elements in the rhizosphere sediments of *Phragmites australis*. However, in the rhizosphere sediments of *Spartina alterniflora*, Rb and Zr have a good correlation with other elements. In the rhizosphere sediments of *Scirpus mariqueter*, Rb and Zr also showed some correlation with other elements. This may be due to the effect of selective adsorption of heavy metals by different plant roots or other environmental factors. The specific mechanism needs further investigation and verification.

Table 1: Correlation analysis of heavy metal elements in the rhizosphere sediments of *Phragmites australis.*

| | Cu | Fe | Mn | Ni | Pb | Zn | Rb | Sr | Zr | Cr |
|---|---|---|---|---|---|---|---|---|---|---|
| Cu | 1 | .906** | .830** | .665* | .762** | .900** | .755** | .459 | .030 | .345 |
| Fe | | 1 | .905** | .887** | .726* | .982** | .581 | .505 | .183 | .649* |
| Mn | | | 1 | .798** | .624* | .851** | .608* | .608* | .173 | .421 |
| Ni | | | | 1 | .449 | .886** | .365 | .388 | .302 | .818** |
| Pb | | | | | 1 | .744** | .550 | .567 | .451 | .262 |
| Zn | | | | | | 1 | .549 | .424 | .238 | .627* |
| Rb | | | | | | | 1 | .679* | .145 | .044 |
| Sr | | | | | | | | 1 | .397 | .228 |
| Zr | | | | | | | | | 1 | .227 |
| Cr | | | | | | | | | | 1 |



Table 2: Correlation analysis of heavy metal elements in the rhizosphere sediments of *Scirpus mariqueter.*

| | Cu | Fe | Mn | Ni | Pb | Zn | Rb | Sr | Zr | Cr |
|---|---|---|---|---|---|---|---|---|---|---|
| Cu | 1 | .954** | .941** | .856** | .833** | .979** | .824** | .342 | .622* | -.007 |
| Fe | | 1 | .954** | .892** | .839** | .980** | .790** | .295 | .705* | .179 |
| Mn | | | 1 | .770** | .732* | .953** | .729* | .175 | .523 | -.002 |
| Ni | | | | 1 | .929** | .883** | .807** | .404 | .804** | .267 |
| Pb | | | | | 1 | .866** | .704* | .333 | .899** | .112 |
| Zn | | | | | | 1 | .759** | .275 | .690* | .050 |
| Rb | | | | | | | 1 | .687* | .578 | .122 |
| Sr | | | | | | | | 1 | .357 | .291 |
| Zr | | | | | | | | | 1 | .299 |
| Cr | | | | | | | | | | 1 |

Table 3: Correlation analysis of heavy metal elements in the rhizosphere sediments of *Spartina alterniflora.*

| | Cu | Fe | Mn | Ni | Pb | Zn | Rb | Sr | Zr | Cr |
|---|---|---|---|---|---|---|---|---|---|---|
| Cu | 1 | .986** | .975** | .981** | .946** | .992** | .968** | .731* | .909** | .207 |
| Fe | | 1 | .980** | .990** | .954** | .996** | .954** | .745** | .924** | .192 |
| Mn | | | 1 | .971** | .947** | .983** | .907** | .702* | .921** | .168 |
| Ni | | | | 1 | .933** | .988** | .957** | .784** | .910** | .175 |
| Pb | | | | | 1 | .961** | .909** | .731* | .977** | .294 |
| Zn | | | | | | 1 | .956** | .740** | .924** | .211 |
| Rb | | | | | | | 1 | .783** | .892** | .125 |
| Sr | | | | | | | | 1 | .724* | .183 |
| Zr | | | | | | | | | 1 | .215 |
| Cr | | | | | | | | | | 1 |

## 6 CONCLUSIONS

Through the analysis of the changes of heavy metal in the rhizosphere sediments of different vegetations on the tidal flats of the Minjiang River estuary, it is found that the heavy metals in the rhizosphere sediments of *Phragmites australis*, *Scirpus mariqueter* and *Spartina alterniflora* were significantly enriched at the depth of 2 cm. In the rhizosphere sediments of *Phragmites australis* and *Scirpus mariqueter*, heavy metal is also enriched at the depth of 10~12cm.

Because the root system of *Spartina alternifolia* is more developed than those of *Phragmites australis* and *Scirpus mariqueter*, and it has a stronger adsorption capacity for heavy metals in surface sediments. It resulted in the fact that *Spartina alterniflora* did not show similar heavy metal accumulation to those of *Phragmites australis* and *Scirpus mariqueter* at the depths of 10~12 cm.

The content of heavy metals in the rhizosphere sediments of *Scirpus mariqueter* was the lowest at the depth of 16 cm, and then shows increasing with depth. It is inferred that the adsorption of heavy metals by the roots of *Scirpus mariqueter* is mainly concentrated at the depth of 16 cm.

The correlation analysis of the 10 heavy metal elements indicates that there are strong correlations among Cu, Fe, Mn, Pb, and Zn. It can be speculated that they have similar sources and may have a certain relationship with human activities. Cr, Sr is more likely to come from natural sources. Rb, Zr may be significantly affected by the selective adsorption of different plant roots or other environmental factors.

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