Assessment of Nutrient and Heavy Metal Pollution in Channel Dredged Sediments in the middle and lower reaches of the Yangtze basin

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Abstract: There was a large amount of dredged materials produced stably in the Yangtze waterway each year. How to dispose these dredged materials was a major technical problem in the field of port and waterway engineering. The dredged materials were valuable resource, and the utilization of dredged materials in landscape can be an important direction in the future. To analyze the feasibility of dredging for landscaping, the waterway dredged sediments from middle and lower reaches of the Yangtze River basin, such as Dongting Lake, Chenglingji section, Zhenjiang section, Nantong section and Taihu Lake were collected, and the nutrient characteristics, heavy metal content and pollution degree were analyzed. The results showed that the pH, moisture content, petroleum hydrocarbons, organic matter and available P in Yangtze River waterway dredging sediments were 7.28~7.74, 3.75~28.27%, 14.21~121.84 ppm, 1.88~5.29% and 16.96~65.38 ppm respectively, which were moderate pollution and suitable for plants growth. The content of available N and available K content were 67.12~87.97 ppm and 2.78~20.11 ppm, which were too low to meet the needs of plant growth. Extra sources of nitrogen and potassium should be added into the sediments when reused. Dredged sediments were contaminated by heavy metals Cu, Pb and Zn, the evaluation results showed that their enrichment effect was not obvious, which won't affect the sediment utilization. Dredged sediments were widely contaminated by Cd (0.05~2.68 mg/kg), and there was a certain enrichment effect, so some Cd hyperaccumulators should be planted to remediate Cd in dredged sediments.

1 Introduction

Dredging was necessary to create and maintain navigation channels for harbors and waterways. Billions of cubic yards of sediments were dredged each year. At a rough estimate, inland port and waterway engineering in China could produce 70~90 million cubic metres of dredged sediments each year[1].

Due to the constant input of the land-sourced pollutants and discharge of pollutants from waterway transportation itself to the river, dredged sediments from inland river were polluted by heavy metals (Yi Y et al, 2011), nutrients (like nitrogen and phosphorus) and refractory organic matter [2]. Heavy metals in dredged sediments were often considered as conservative pollutants [3,4], which could cause potential threat to ecosystems [5, 6].

Traditionally, dredged sediments were hydraulically raised and placed in confined disposal facilities [7]. Dredged sediments were rich in nutritive organic matters and could be used for surface soil enhancement rather than discarded as spoil material[8]. The Toledo-Lucas

County Port Authority (TLCPA) was currently leading an effort to plan for the full-scale implementation of beneficial use of dredged materials for agricultural and blended soil product purposes.

Yangtze River as the first river running through east and west China, which connecting the southwest, central, east three major economic zones to be a transportation artery. Yangtze River flowed across downtown with dense population and heavy industrialization and was affected by seriously industrial and domestic pollution, which had resulted in poor water quality in the estuary [9].

This study took the waterway dredged sediments from middle and lower reaches of the Yangtze River basin, such as Dongting Lake, Chenglingji section, Zhenjiang section, Nantong section and Taihu Lake as the research objects, and referred to the classification standard of soil nutrient elements as well as sediment background value of Yangtze River stream, to analyze and evaluate the nutrient and heavy metal pollution characteristics of the Yangtze River waterway dredging sediments, which would provide a scientific basis for recycling utilization of waterway dredged sediments.

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2 Materials and methods

2.1. Sample collection

To investigate and verify the nutrient characteristics, heavy metal content and pollution degree in the dredged sediments of Yangtze River basin, Dongting Lake, Chenglingji section, Zhenjiang section, Nantong section and Taihu Lake were selected as the show study areas, which were shown in Figure 1.

The sediment samples were collected in November

2013 (rain season) and August 2014 (dry season). 1 kg sediment was sampled in each point. Sampled sediments were stored in a clean PE sealing bag, and then putted in a foam box with ice packs at the bottom. The foam box full of sediments were carried back to the laboratory within 24 h and then stored in refrigerator or determined immediately. Sediment samples were pretreated as follows: air-dried, removed the stones, animal and plant residues and other foreign matters in it, grinded, sifted through a 100 mesh sieve, and then placed in a dry condition.

Figure 1. Sampling locations of the dredged sediments in the channel of Yangtze River (a); the general location of sampling sites of each area (b) (c).

2.2 Testing items and methods

The physical and chemical properties of dredged sediments were analyzed, including plant nutrients,

pollution relevant as well as other properties. Specific analysis indicators, methods and significance were shown in Table 1.

Table 1. Physico-chemical properties analysis parameters and methods of dredged materials.

Analysis Index	Analysis Methods	Analysis Meaning [10]
pH	Potentiometry	Closely related to the biological effectiveness of heavy metals and nutrients
Petroleum hydrocarbons	N-Hexane extraction – spectrophotometric colorimetry	One of the main pollutants in the channel
Organic matter	Potassium dichromate oxidation - ferrous sulphatetrimetry	The main carrier of plant nutrients, and an important index of soil fertility
Available N	Alkaline hydrolysis diffusion	The nitrogen that can be directly used by plants
Available P	NaHCO ₃ leaching-molybdenum antimony	An index representing the ability of soil to

Available K	colorimetry Ammonium acetate extraction - atomic absorption spectrophotometry	supply Available P An index representing the ability of soil to supply Available K
Heavy metals	Digested by HNO ₃ +HClO ₄ , measured by ICP-MS	The mainly concerned pollutants

2.3 Evaluation standards and methods

2.3.1 Evaluation standard of dredged sediments for nutrient characteristics.

Indicators such as organic

Table 2. Soil nutrient classification standard in China.

Levels	Organic matter (%)	Available N (ppm)	Available P (ppm)	Available K (ppm)
1 very rich	>4	>150	>40	>200
2 rich	3~4	120~150	20~40	150~200
3 moderate	2~3	90~120	10~20	100~150
4 lack	1~2	60~90	5~10	50~100
5 very lack	0.6~1	30~60	3~5	30~50
6 stunning lack	<0.6	<30	<3	<30

2.3.2. Analysis and evaluation of dredged sediments for heavy metal pollution.

The heavy metals Pb, Cd, Cu,

matter, available nitrogen, phosphorus and available potassium were graded and evaluated referring to the classification standard of soil nutrients (see Table 2).

and Zn were selected to assess the sediment quality of the eight situations. The reference values of heavy metals (Z et al, 1990) were shown in Table 3.

Table 3. Reference values of heavy metals.

Heavy metals	Cu	Pb	Zn	Cd
The first grade standard values of soil environmental	35.0	35.0	100	0.20
China soil environmental background values	22.6	26.0	74.2	0.097
Yangtze River stream sediment background value	21.5	21.4	73.6	0.15

Geoaccumulation index and single-factor pollution index were the two methods that mostly used as quantitative determination of the potential hazardous trace elements pollution in aquatic sediment.

The single factor index method could be expressed as formula (1):

$$P_i = \frac{C_i}{S_i} \quad (1)$$

where P_i was the pollution index of heavy metal i ; C_i

(mg/kg) was the actual monitoring data of heavy metal i ; S_i (mg/kg) was the environmental background value at Nanjing City region.

According to the relation between the evaluation indexes and the contamination degree, sediment pollution was divided into 4 grades (Table 4).

Table 4. Relation between the evaluation indexes and the contamination degree.

Evaluation Indexes	<1	1~3	3~6	≥6
Contamination Degree	Slight Contaminated	Moderate Contaminated	Heavy Contaminated	Extremely Contaminated

Geoaccumulation index (IG) method proposed by Müller was a quantitative research method on heavy metal pollution levels in sediment (especially sediment of aquatic environment) that reflects pollution level by evaluating heavy metal content in sediment. It can reveal the enrichment degree of heavy metals in sediment [11], and considered the influence of man-made pollution factors and natural diagenesis on background value, which has been widely adopted [12]. Calculation formula of I_{geo} was showed as formula (2).

$$I_{geo} = \log_2[C_n/(kB_n)] \quad (2)$$

In the above formula,

C_n — measured content of heavy metal n in sediment (mg/kg).

B_n — geochemical background value of heavy metal n of sediment. In this formula were the heavy metals element background values of sediment from Yangtze River stream adopted (mg/kg).

k — modified index being mainly used to correct the change of background value caused by the effects as weathering, and generally take 1.5.

According to the I_{geo} values, pollution degree could be divided into seven grades, as shown in Table 5.

Table 5. Contamination degree corresponding to index of Geoaccumulation.

I _{geo}	<0	0~1	1~2	2~3	3~4	4~5	>5
Grades	0	1	2	3	4	5	6
Pollution Levels	Clear	Clear-moderate	Moderate	Moderate-strong	Strong	Strong-extremely Strong	Extremely Strong

3 Results and discussions

3.1 Physicochemical properties and nutrient characteristics of dredged sediments.

The pH was an important factor for affecting, adjusting and controlling the matter migration of pedosphere. Physicochemical properties and nutrient characteristics of waterway dredged sediments from Yangtze River basin were shown in Table 6. The pH of the dredged sediments from the study areas was between 7.11~7.87, showing weak alkaline, suitable for the growth of most plants. The moisture content was abundant enough to meet the needs of the plant growth.

The quality standard value for petroleum hydrocarbons content of river and lake sediment was referred to the first grade standard values of soil environmental (100mg/kg) in this study. As shown in Table 6, the petroleum hydrocarbon content was between 4.63~121.84 mg/kg. Petroleum hydrocarbon content of sediments from Dongting Lake and Chenglingji Section was higher than other sample areas. Petroleum hydrocarbon content of sediments from Dongting Lake

exceeded the first grade standard values of soil environmental, thus some measures should be taken to control the harmful effect when recycling utilization of dredged sediments. Nevertheless, the petroleum hydrocarbon content of sediment from other sample areas would not affect the utilization of dredged sediments.

The organic matter of dredged sediment was between 0.70~10.10%. For organic matter, sediments from Dongting Lake and Chenglingji Section reached level 1 (very rich), sediments from Taihu Lake reached level 2 (rich), sediments from Zhenjiang section reached level 3 (moderate), and sediments from Nantong section reached level 4 (lack). Consequently, dredged sediments from Dongting Lake, Chenglingji Section, Taihu Lake and Zhenjiang Section could supported landscape application, however, sediments from Nantong Section needed adding extra organic matter to improve the fertility.

The content of available nitrogen in dredged sediment was between 28.98~174.87 mg/kg, and the sediments lacked the available nitrogen; nevertheless, few sampling points in Zhenjiang Section reached a high and above level.

Table 6. Physicochemical and nutrient properties of sediment samples from Yangtze River basin.

	Dongting Lake	Chenglingji Section	Zhenjiang Section	Nantong Section	Taihu Lake
pH	7.61±0.06	7.61±0.16	7.63±0.02	7.74±0.12	7.28±0.27
Moisture content/%	23.87±1.14	23.75±2.85	28.27±1.22	23.92±0.56	25.80±3.44
Petroleum Hydrocarbons /ppm	121.84±91.24	57.74±35.68	26.73±4.63	34.66±5.80	14.21±6.38
Organic matter /%	5.29±0.54	5.15±1.27	2.07±0.46	1.88±0.03	3.41±2.69
Available N /ppm	68.20±6.54	78.88±4.66	67.12±46.57	73.83±0.26	87.97±51.98
Available P /ppm	65.38±26.50	33.59±21.16	22.88±14.99	22.00±1.63	16.96±7.07
Available K /ppm	14.26±2.08	8.31±3.60	16.82±0.62	2.78±0.40	20.11±7.87

The content of available phosphorus in all the dredged sediments was between 7.32~81.82 mg/kg. Average content of available phosphorus in dredged sediments from Dongting Lake reached level 1 (very rich), sediments from Chenglingji Section reached level 2 (rich), sediments from Zhenjiang Section and Nantong Section reached level 3 (moderate), sediments from Taihu Lake reached level 4 (lack), and needed adding additional source of phosphorus when landscape application. It was found that the content of available P in sediments from different sampling points at Dongting Lake and Chenglingji Section presented obviously fluctuations, and the content of available P in sediments from Taihu Lake and Nantong Section presented slightly fluctuations, however, the average content of all stations was at the same level.

The available potassium content in dredged sediments was between 2.37~33.74 mg/kg, and almost all the

sampling points were less than 30 mg/kg, reaching 6 level (stunning lack). The available potassium was an essential element for plant growth, and supplement of available potassium fertilizer was required when sediment used as horticultural application.

3.2 Pollution analysis and ecological risk assessment on heavy metal

3.2.1 Analysis of heavy metal content and contamination level. Figure 2 presented the analysis results of heavy metals in dredged sediments from research area. Concentration of heavy metal Cu was between 1.95~ 62.76 mg/kg, and the average concentration was 23.81 mg/kg; the average content of Cu in dredged sediments from Dongting Lake and Chenglingji Section exceeded

slightly the first grade standard values of soil environmental; and that from Zhenjiang Section was lower than the first grade standard values of soil environmental but higher than the Yangtze River stream sediment background value; and that from the other sampling areas was lower than the Yangtze River stream sediment background value. Variance coefficient of Cu in Chenglingji Section was highest, and Dongting Lake was next, and Nantong Section was the lowest.

Concentration of heavy metal Pb was between 9.56~41.64 mg/kg, and the average concentration was 21.40 mg/kg; Pb concentration of all sampling points were lower than the first grade standard values of soil environmental, but all points of Dongting Lake and Zhenjiang Section, and most points of Chenglingji Section were higher than the Yangtze River stream sediment background value; the rangeability of Pb concentration was generally low except of Chenglingji Section.

Concentration of heavy metal Zn was between 1.65~131.82 mg/kg, and the average concentration was 42.70 mg/kg; Of all the sampling areas, Zn concentration of most points was lower than the Yangtze River stream sediment background value, however, the content of some points of Dongting Lake, and few points of Chenglingji Section was higher than the first grade standard values of soil environmental. The variety range of Zn was generally high except of Zhenjiang Section and Nantong Section.

Cadmium content was between 0.05~2.68 mg/kg, and the average concentration was 0.68 mg/kg; Cd concentration of all research areas exceed the first grade standard values of soil environmental and the Yangtze River stream sediment background value. Furthermore, Cd concentration of Dongting Lake and Chenglingji Section even exceeded the second grade standard values of soil environmental (0.6 mg/kg). The highest concentration appeared in sampling area of Dongting Lake, which was 4.46 times higher than the second grade standard values.

Figure 2. Concentrations of Cu, Pb, Zn and Cd in sediments from different areas.

In summary, Dongting Lake suffered the most serious heavy metal pollution. Chenglingji Section suffered some heavy metal pollution. The concentration of Cd in Taihu Lake exceeded certain limits, but the other heavy metals were low. With respect to Zhenjiang Section and Nantong Section, content of all heavy metals were at a low level. Concentration of heavy metals Cu, Pb and Zn was relatively lower, however, content of Cd was generally high. Therefore, pollution of Cd was respected to be treated.

3.2.2 Assessment of heavy metal pollution. Evaluation result of single factor pollution index method was shown in Figure 3. With regard to heavy metal Cu, pollution index of almost all sample points in Dongting

Lake, and Zhenjiang Section was among 1~3, being in the medium pollution level; pollution indexes of all samples from Taihu Lake and Nantong Section were less than 1, being low pollution levels; pollution level of each study area arranging from high to low was respectively Chenglingji Section > Dongting Lake > Zhenjiang Section > Taihu Lake > Nantong Lake. With respect with Pb: pollution index of all sample points in Dongting Lake, Zhenjiang Section and most of the sampling points in Chenglingji Section was in the range of 1~3, being in the medium pollution level; pollution index of all samples from Nantong and most of the samples from Taihu Lake was below 1, being in low pollution level; pollution level of each study area arranging from high to low was respectively Dongting Lake > Zhenjiang

Setion>Chenglingji Section >Taihu Lake > Nantong Lake. Regarding Zn: pollution index of all samples from Dongting Lake and some samples from Chenglingji Section was among 1~3, being in certain pollution levels; pollution index of all samples from the other study areas was all below 1, being in low pollution level; pollution level of each study area arranging from high to low was respectively Dongting Lake>Chenglingji Section >Taihu Lake > Zhenjiang Setion> Nantong Lake. As to Cd, pollution index of all samples from Dongting Lake and

most samples from Chenglingji Section reached to 6, being in serious pollution level; pollution index of a few samples from Chenglingji Section and most samples from Chenglingji Section, Zhenjiang Section and Taihu Lake was in the range of 1~3, being in medium pollution levels; pollution index of all samples from Nantong Section was all below 1, being slightly polluted; pollution level of each study area arranging from high to low was respectively Dongting Lake>Chenglingji Section > Zhenjiang Setion>Taihu Lake > Nantong Lake.

Figure 3. Single factor index (C_f^i) of Cu, Pb, Zn and Cd in sediments from different areas.

Note: dotted lines in figures represent classification boundaries of the single factor index, and the detailed classification standard are showed in Table 4.

The cumulative index evaluation results were shown in Table 7. In the study area, excepting of individual points that were subjected to moderate pollution by Cu, Pb and Zn, other sampling points were all clear with the three heavy metals. Apart from Nantong Section, there existed varying degrees of Cd contamination in other sampling regions. The sediments from Taihu Lake suffered a stronger degree of Cd pollution, and sediments from Chenglingji Section suffered a moderate – strong level of Cd pollution. Overall, enrichment effects of Cu, Pb and Zn pollution in study areas of Yangtze River were generally lighter. However, enrichment effect of Cd pollution in midstream of Yangtze River like Taihu Lake and Chenglingji Section was rather serious, but that in middle and downstream such as Zhenjiang Section, Nantong Section and Taihu Lake was not critical.

Evaluation results showed that pollution of Cu, Pb and Zn in Dongting Lake and Chenglingji Section was moderate level, but Cd was serious. Cu, Pb and Cd of pollution in Zhenjiang Section was moderate level, but

Zn was not obvious. Pollution of all analyzed heavy metals in Taihu Lake and Nantong Section was rather lower. There existed a certain enrichment effects in midstream of Yangtze River like Dongting Lake and Chenglingji Section. Chenglingji was located in the mouth of East Dongting Lake, which was in middle and downstream of Yangtze River, belonging to Yueyang City. Chenglingji port was a national port, there were many industrial enterprises such as thermal power plant, paper mill, smelting factory, petrochemical corporation surround near the port. The sediment in the Chenglingji port was polluted by domestic sewage, industrial wastewater and ship oil-containing wastewater. So the Cd pollution in Chenglingji was the most serious.

Table 7. *Igeo* and Pollution levels of Cu, Pb, Zn and Cd in sediments from different areas.

		Research areas					
		Dongting Lake	Chenglingji Section	Zhenjiang Section	Nantong Section	Taihu Lake	Mean
Cu	Max	0.53/1	0.96/1	-0.14/0	-3.72/0	-0.91/0	-0.66/0
	Min	-0.20/0	-0.85/0	-0.61/0	-4.05/0	-1.57/0	-1.46/0
	Mean	0.21/1	0.32/1	-0.36/0	-3.87/0	-1.20/0	-0.98/0
Pb	Max	-0.09/0	0.38/1	-0.09/0	-1.27/0	-0.57/0	-0.33/0
	Min	-0.32/0	-1.75/0	-0.40/0	-1.73/0	-1.44/0	-1.13/0
	Mean	-0.20/0	-0.33/0	-0.23/0	-1.53/0	-1.10/0	-0.68/0
Zn	Max	0.26/1	0.10/1	-3.96/0	-6.03/0	-0.77/0	-2.08/0
	Min	-0.31/0	-2.10/0	-4.36/0	-6.06/0	-4.88/0	-3.54/0
	Mean	0.01/1	-0.62/0	-4.15/0	-6.05/0	-2.24/0	-2.61/0
Cd	Max	3.57/4	3.21/4	0.22/1	-2.22/0	0.21/1	1.01/2
	Min	2.08/3	0.09/1	-1.19/0	-2.32/0	-1.22/0	-0.51/0
	Mean	3.01/4	2.37/3	-0.32/0	-2.26/0	-0.33/0	0.49/1

4 Conclusion

(1) The pH and moisture content of dredged sediments in the Yangtze River basin could meet the requirements of most of the plants growth. The content of petroleum hydrocarbon was generally out of limit for sediments from Dongting Lake. However, petroleum hydrocarbon of the other study areas would not influence the resource disposal of sediments.

(2) Organic matter content in Dongting Lake, Chenglingji Section, Taihu Lake and Zhenjiang Section all can satisfy the landscape use; however, organic matter in Nantong Section was slightly lower, and appropriate organic fertilizer should be added in the sediment to preserve soil fertility. Available N and K were widespread low in most of research areas, so additional source of N and K should be added to ensure the normal growth of plants for phytoremediation. Apart from individual sample points, available P could satisfy most plants growth.

(3) Although the dredged sediments from Yangtze River basin suffered varying degrees of Cu, Pb and Zn pollution, it can meet the requirement of resource utilization because the enrichment effects was not obvious. However, Cd pollution was generally serious, and had a certain concentration effect. Therefore, plants for phytoremediation should be planted to reduce Cd content in dredged sediments.

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