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Quality Status and Ecological Risk Assessment of Xixi Wetland's Sediments

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The soil characteristics and content of heavy metal and persistent organic pollutants in Hangzhou Xixi wetland's sediments were tested and researched and the ecological risk of wetland's sediments was assessed by using index of single factor and HaKanson index method. The results showed that average content of sediments' heavy metal was lower than the secondary standard of Soil Environment Quality Standard (GB15618-1995). Taking Zhejiang province soil background values for risk assessment, the pollution degree of each monitoring point was medium ecological harm. The possible heavy metal source of sediments was discussed and the corresponding protective measures were putting forward.

Keywords: Xixi wetland, Soil characteristic, Heavy metal, Persistent organic pollutants, Risk assessment.

INTRODUCTION

With a variety of functions and values, wetland ecosystem as an important natural resources, known as the "kidneys" of the nature. It plays an important role in regulating climate, pollutants degradation, purifying water, conservation of biodiversity and providing production living resources for human, *etc*[1].

Xixi wetland is a national wetland park integrated with urban wetland, farming wetland and hydrology wetland. It's located in west of Hangzhou, east to Zijin port, west is bounded by Wuchang port and Yuhang district, south to Yanshan river, north to Yuhangtang river, only 5 km far away from west lake. Historically, Xixi had once known as the 'vice west lake'. The best of Xixi is the water. The creek, reed, willow, fish, persimmon, bamboo and water chestnut constitutes a unique rural landscape of Jiangnan. Xixi wetland is covered about 50 % area by water, as well as a huge amount of total surface water. It has a dense river network, high coverage of surface water and many ponds. With the advancement of industrialization and urbanization, Xixi wetland has degradated seriously[2], the area drops from 60 km^2 to 10 km^2.

The protection of Xixi wetland is imminent. Sediment, one of three most important factors of wetland water body (including water quality, aquatic organism and sediment), is the habitat of benthos and aquatic plant. As an important storage of nutriment, sediment plays a vital function in the aspect of precipitating and releasing the pollutants. This article investigated, analyzed and evaluated the Xixi wetland's sediment and the corresponding protective measures are putting forward as to offer a scientific basis to the future management and policy making of wetland.

EXPERIMENTAL

Based on Technical Manual of Monitoring Surface Water and Wastewater (HJ/T 91-2002), a national environmental protection industry standards, we pointing and sampling the water[3]. Referenced related research achievements of Xixi wetland in ecology, biology, geology and climatology; selected different environmental forms such as watercourse, farmland, shallow swamps, artificial pond, layland and construction land; based on the degree of interference, the protection measures taken and the planning, we totally sampled 7 survey samples in the wetland (Table-1).

The samples were taken using the Beeker sediment sampler and kept away from the river-bed scour, sedimentary instability, grass and surface susceptible to stir. The samples were sealed with polyester bags after stratification, noted and then sent back to the lab in time. The ones were air-dried at low temperature, levigated, then sieved with 2 mm griddle and mixed, as for physical analysis. An other part of the samples milled 2 mm hole sieve were further levigated through 100 mesh sieve, as for chemical analysis. All the samples were

TABLE-1
GENERAL SITUATION OF SAMPLES

Number	Interference type of water	Interference type of precipitation
1#	Closed aquifer (dry pond in 2011)	Dry pond in 2011
2#	Watercourse, unnavigable (small boats sometimes)	Not dredging
3#	Semi-closed aquifer (connected with watercourse)	None
4#	Drainage line, navigable (water from the Qiantang River)	Dredging in 2011
5#	Closed aquifer (not dry)	None
6#	used to be farmland surrounded	None
7#	Branch of watercourse	Not dredging

kept in bottle, analyzed based on Analysis Method of Soil Agricultural Chemistry (analysis on sediment is similar to soil)[4]. The main monitor index would be soil texture, geochemistry index, heavy metal and persistent organic pollutants.

Analytical method: Phosphorus (molybdenum antimony colorimetric method); organic matter (potassium dichromate solution method); pH (electrode method); total nitrogen (Kieldahl's method); soil particle composition-size distribution (hydrometer method); CEC (EDTA-ammonium salt rapid method); total mercury and total arsenic (cold atomic fluorescence spectrometry); total zinc (Flame atomic absorption spectrophotometry); chromium, copper, cadmium and lead (Inductively coupled plasma-mass spectrometry, US EPA 200.8-1994); persistent organic pollutants (gas chromatography or gas chromatograph-mass spectrometer).

Ecological risk assessment methods: Using single factor method, calculating formula is:

$$C_i = \frac{c^i}{c^i_n}$$

C_i is contamination index; C^i is the measured concentration; c^i_n is reference value or standard value and that we use Zhejiang province soil background values instead because of no uniform standard yet. $C_i < 1$ means that sediment is not polluted, $C_i \geq 1$ means that sediment is polluted and the bigger, the worse sediment polluted.

According to the properties and environmental behavior characteristics of heavy metals, HaKanson index method was put forward[5], which is an evaluating method based on sedimentology. It not only take the soil heavy metal content into account, but also combine the ecological and environmental effect of heavy metals, with comparable equivalent index classification method. Index method of potential ecological harm is one of widely used heavy metal pollution assessment methods, it combine bio-toxicology, environmental chemistry and ecology, distinguish the degree of potential ecological harm of heavy metal elements by quantitative method. To evaluate possible ecological risk of heavy metals, the calculating formula of potential ecological risk index of single metal is:

$$E_i = T_i \times C_i$$

T_i is biological toxicity response factor, which reflects the harm of heavy metals to human and ecological system. The order of toxic response coefficient for 7 kind of heavy metal is as follows: Hg(40) > Cd(30) > As(10) > Pb = Cu(5) > Cr(2) > Zn(1).

The calculating formula of potential risk index (RI) of a variety of pollutants is:

$$RI = \sum_{i=1}^{n} E_i$$

Correlation of E_i and RI is shown in Table-2.

TABLE-2
POTENTIAL ECOLOGICAL RISK EVALUATION STANDARDS OF HEAVY METAL POLLUTION

Contamination factor (E_i)	Contamination index (RI)	Degree of contamination
≤ 40	≤ 150	Light
40-79	150-299	Medium
80-159	300-600	Strong
160-320	> 600	Very strong
> 320	–	Pole-strong

RESULTS AND DISCUSSION

Soil characteristic of sediment: The samples were taken using the Beeker sediment sampler from Netherlands Eijkelkamp Company. The sensory index and physical and chemical indicators were evaluated, including research on soil characteristics of the sediment (basic physical property index, water content, size distribution, denseness and mineral composition) and study on geochemistry index of the sediment (mensuration of the solid content, organic content, main physical and chemical properties, pH and REDOX potential, *etc*).

(1) Soil characteristics of Xixi wetland's sediment: Result of the research and analysis are shown in Table-3; (2) Study on geochemistry index of the sediment: Result of the research and analysis are shown in Table-4.

Sediment pollution investigation: (1) Result of the wetland's heavy metal analysis is shown in Table-5. (2) Persistent organic pollutants (POPs).

PCBs and other persistent organic pollutants in sediment were tested. The results show that PCBs are not detected and

TABLE-3
ANALYSIS OF SOIL CHARACTERISTICS OF Xixi WETLAND'S SEDIMENT

Number	D < 0.002 (%)	0.002 < D < 0.02 (%)	0.02 < D < 0.2 (%)	0.2 < D < 2 (%)	Sand level content (%)	Water content (%)
1	29.35	28.31	37.45	4.89	70.65	2.0
2	33.43	29.89	34.07	2.61	66.57	2.2
3	29.98	31.20	35.02	3.80	70.02	2.4
4	33.46	24.95	36.28	5.31	66.54	3.0
5	26.08	30.53	38.06	5.33	73.92	3.4
6	32.14	27.66	34.31	5.89	67.86	1.3
7	27.87	31.59	35.77	4.77	72.13	5.1

Note: D < 0.002 is clay, 0.002 < D < 0.02 is gravel, 0.02 < D < 0.2 is fine sand, 0.2 < D < 2 is coarse sand grains. The unit of diameter is mm

TABLE-4
ANALYSIS OF GEOCHEMISTRY INDEX OF Xixi WETLAND'S SEDIMENT

Number	Total phosphorus (g/kg)	pH	Organic content (g/kg)	CEC (cmol (+)/kg)	Total nitrogen (g/kg)
1	1.316	7.18	0.139	13.39	1.21
2	0.972	6.17	0.157	13.20	1.17
3	0.852	5.58	0.193	9.96	1.27
4	0.966	7.50	0.057	14.56	0.67
5	0.504	6.44	0.241	12.57	1.47
6	0.246	5.96	0.146	9.65	0.89
7	0.654	7.10	0.251	13.84	1.49

TABLE-5
HEAVY METAL CONTENT OF Xixi WETLAND'S SEDIMENT (mg/kg)

Item	Hg	As	Zn	Cr	Cu	Cd	Pb
AVG	0.17	5.58	110.50	66.70	31.10	0.14	33.30
Maximum	0.25	7.73	132.00	73.80	33.70	0.17	40.90
Minimum	0.12	2.09	87.40	59.00	27.40	0.09	19.80
Median	0.17	5.60	110.00	69.80	30.60	0.15	35.90
SD	0.05	1.83	15.13	6.42	2.40	0.03	8.58
CV (%)	28.89	32.84	13.69	9.62	7.72	21.77	25.76
Background Value	0.07	7.50	62.10	49.70	15.00	0.06	22.40
Standard value	0.50	30.00	250.00	200.00	200.00	0.30	300.00

Note: CV = SD/AVG × 100 %; background value is Zhejiang province soil element background values[6]; standard value is secondary standard of Eviron-ental Quality Standard for Soils (pH: 6.5-7.5)[7]

indicating that there is no risk of PCBs pollution. The results of testing polycyclic aromatic hydrocarbons (PAHs) are shown in Table-6 and Fig. 1.

TABLE-6
PAHS CONTENT OF SEDIMENT (µg/kg)

Compound	Minimum	Maximum	AVG
Na	15	42.4	25.9
Flu	7.3	12.7	9.8
Phe	25.8	63.2	44.5
An	1.5	3.2	2.13
Fl	10.1	27.1	20.8
Pyr	9.1	29.6	18.8
BaA	nd	9.5	7.8
Chr	3.3	10.8	7.43
BbF	7.1	21	15.5
BkF	2.3	19.5	8.93
BaP	2.4	9.8	5.3
DBA	nd	18.5	8.05
BghiP	nd	12.1	8.4
Ip	5.6	12.8	10.3
Total PAHs	89.5	292.2	193.64

nd: not detected

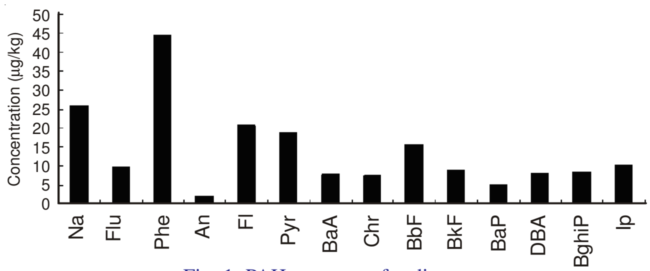

Fig. 1. PAHs content of sediment

Ecological risk assessment analysis: Result calculated with single factor method is shown in Table-7.

From the aspect of single factor pollution index, order for 7 kinds of pollution elements is Hg > Cd > Cu > Zn > Pb > Cr > As. Thought comparison of the contamination index for different metals, it has been shown that one single metal has different representation in different monitoring point. For example, Hg shows contamination index value of 3.85 in 3# monitoring point, while 1.85 in 1# and 7#. The pollution degree of As in the sediment is lowest and each monitoring is not polluted except 7#. Different heavy metals has different representation in one monitoring point, such as Cd > Cu > Zn > Hg > Pb > Cr > As in 1#.

TABLE-7
SINGLE FACTOR RISK INDEX (C_i) OF HEAVY METALS

Monitoring point	Hg	As	Zn	Cr	Cu	Cd	Pb
1	1.85	0.74	1.88	1.43	2.25	2.59	1.8
2	3.23	0.83	1.98	1.48	2.21	2.93	1.81
3	3.85	0.75	1.41	1.19	1.83	2.24	1.42
4	2.77	0.94	1.71	1.46	2.04	1.55	1.6
5	2.31	0.64	1.77	1.21	1.94	2.76	1.83
6	2.61	0.28	1.58	1.22	2.04	1.72	1.06
7	1.85	1.03	2.13	1.4	2.23	2.59	0.88
AVG	2.64	0.74	1.78	1.34	2.08	2.34	1.49

TABLE-8
POTENTIAL ECOLOGICAL RISK INDEX OF HEAVY METALS IN SEDIMENT

Monitoring point	E_i							RI
	Hg	As	Zn	Cr	Cu	Cd	Pb	
1	74.00	7.40	1.88	2.86	11.25	77.70	9.00	184.09
2	129.20	8.30	1.98	2.96	11.05	87.90	9.05	250.44
3	154.00	7.50	1.41	2.38	9.15	67.20	7.10	248.74
4	110.80	9.40	1.71	2.92	10.20	46.50	8.00	189.53
5	92.40	6.40	1.77	2.42	9.70	82.80	9.15	204.64
6	104.40	2.80	1.58	2.44	10.20	51.60	5.30	178.32
7	74.00	10.30	2.13	2.80	11.15	77.70	4.40	182.48
AVG	105.54	7.44	1.78	2.68	10.39	70.20	7.43	205.46

Evaluation index of heavy metals pollution in sediment is shown in Table-8.

From the aspect of RI, order for 7 kinds of pollution elements is Hg > Cd > Cu > As > Pb > Cr > Zn. This is difference from single factor pollution index because some element may has higher contaminated degree, but more affinity to particle, easier to be transferred into sediment by SS, lower its toxicity to creature, so as to lower its potential ecological risk.

From the aspect of a variety of potential risk index, sediment of Xixi wetland belongs to medium ecological harm. From one single monitoring point, ecological risk index (E_i) of As, Zn, Cr and Pb in different monitoring point is lower than 40, it belongs to light ecological harm. Ecological risk index of Cd is among 46.5-87.9, which belongs to medium ecological harm except 2# and 5# is strong, while Hg 80-159, the other nonitoring point belongs to strong except 1# and 7# is medium. For the RI in different points, the order is as follows: 2# > 3# > 5# > 4# > 1# > 7# > 6#. The pollution levels of the monitoring are all medium ecological harm.

Effect of wetland conservation time difference to the contaminants content: Impact of human activities is a vital factor besides the soil background different. The ecological environment had been broken 10 years ago, since the upstream of wetland polluted by industrial and agricultural pollution, water carrying heavy metals into the soil by contact with wetland's soil. In recent years, quality of the wetland had been improved in a certain extent due to the conservation works. The distribution of sediment pollutant is closely related with human activity disturbance intensity. The higher pollutants content point mainly located in the periphery of conservation project while the lower center. Comparison of the RI value of 1# and 5#, because of the dry pond work in 2011 at 1#, the pollution level at 1# is lower than 5#. Monitoring point within the conservation project has a lower ecological risk index.

Effect of different water interference types to the contaminants content: Water type also has an impact on heavy metal content of sediment. From the perspective of the distribution of heavy metals in sampling points 3 and 5, it has been observed that closed water ecological risk degree is lower, semi-closed water is connected with watercourse which provides conditions for the migration of pollutants. In comparison with the distribution of heavy metal in sampling point 2 and 4, because point 4 had experienced the conservation projects such as introducing water from the Qiantang River and dredging, its environmental quality is better than point 2 and its potential risk level is closed to point 7.

Relativity of heavy metals content in sediment: Significantly and extremely significant correlation between elements means that elements have the homologous relationship generally or compound pollution[8-10]. The study on the relativity of heavy metals content can infer whether the heavy metals have the same source. Significantly correlation shows that the heavy metals may have the same source, otherwise, sources might be more than one.

Table-9 shows the relativity analysis on different heavy metals in soil, indicating that only Cu-Zn and Cu-Cr have the significant relativity, that is to say, there may be the same source for Cu, Zn and Cr while others' sources might be more than one.

Artificial source of heavy metals has many types, for example, Zn is often referred to as identify elements of traffic sources[11]. Xixi wetland located in the downtown and surrounded by busy transportation, which do have an effect on the accumulation of Zn element in sediment. Because Xixi wetland used to be dominated by agriculture, abuse of mercury pesticide and copper additive of feed contributed to the soil heavy metal pollution[12], especially Hg and Cu. Moreover, sewage discharge of industrial enterprise zones and residents living quarters at upper stream do effect the accumulation of heavy metals in sediment.

TABLE-9
RELATIVITY OF HEAVY METALS CONTENT IN SEDIMENT

Elements	Hg	As	Zn	Cr	Cu	Cd	Pb
Hg	1.000						
As	-0.088	1.000					
Zn	-0.647	0.549	1.000				
Cr	-0.285	0.638	0.708	1.000			
Cu	-0.618	0.331	0.860*	0.811*	1.000		
Cd	-0.168	0.265	0.580	0.156	0.353	1.000	
Pb	0.152	0.067	-0.019	0.221	-0.030	0.364	1.000

Note: The data marked by asterisk means significant relativity at the level of 0.05

Conclusions and suggestions: The average value of heavy metals from Xixi wetland sediment is lower than the secondary standard for Soil Environmental Quality Standard (GB 15618-1995). However, Except for as, the average value of the rest elements are higher than the soil background values in Zhejiang Province of China, so the soil environmental protection is still need to be strengthen. The method of single factor risk index and potential index being used in the sediment evaluation, different results appeared respectively. The former is suitable for concrete analysis of single metal, while the latter was more suitable for comprehensive evaluation of many kinds of metals.

After several years of planning and renovation, ecological restoration, the environment water quality of Xixi Wetland has improved. However, the pollution sources still exist, there still be many obstacles on the road of wetland environmental protection. Some ideas and ways to protect wetlands environment are suggested as follows:

(1) To establish a monitoring system for ecological models to observe and study the various types of organism, in order to facilitate a timely protection.

(2) **Overall planning and rational layout:** Constantly adjusting and optimizing industry layout surrounding the Xixi wetland, reasonably using and distributing resources.

(3) **Public participation:** To intensify propaganda and popularize wetland environmental protection education and to let urban residents participate in management planning of Xixi wetland.

(4) **Sediment dredging:** To dredge the areas where have intensive original inhabitants and the existing ponds where have poor water quality.

(5) **Ecological aquaculture:** Through site survey, sampling and analysis, to bread native filter-feeding fishes and the fishes, snails, clams and other mollusks which ingest benthic animals into some of the almost enclosed water bodies; arranging certain animal species, formatting a compound three-dimensional cultivation, reducing water pollution and promoting the ecological balance.

In this paper, the value used in the risk analysis is the background value from soil element in Zhejiang Province. While taking Xixi wetland sediment as the basis of ecological risk of heavy metal pollution, the results will have more pertinence and guiding significance. For this reason, it needs to strengthen the research of basic value such as sediment background value, *etc*. Different migration patterns and sedimentary process will affect the final evaluation of the ecological risk of heavy metals. Furthermore, different lakes and rivers have different water quality condition and hydrological characteristics. Therefore, in order to have a more comprehensive understanding, we should strengthen the study of contamination migration and sedimentation in Xixi wetland area.

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