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Determination of Nitrogen and Phosphorus Pollution in River Water and the Effect of Vegetation Buffer Zone on Control

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Abstract: In this paper, based on the analysis and testing of nitrogen and phosphorus content in sediments and interlacing water of Shiwuli River in Chaohu Lake, the form, distribution characteristics and biological availability of nitrogen and phosphorus in sediments were analyzed. Suitable herbaceous vegetation was selected. Through laboratory hydroponic experiments, the removal ability of different plants to nitrogen and phosphorus nutrients was compared and analyzed, and the best plants in riparian buffer zone were determined. Finally, according to the test site topography, six artificial riparian buffer zones with different vegetation patterns were constructed, and field tests were conducted in the form of simulated rainfall to analyze the inhibition effect of vegetation buffer zones with different vegetation patterns and different widths on nitrogen and phosphorus in agricultural non-point source pollution.

1. Introduction

Chaohu Lake is one of the five largest freshwater lakes in China, in the central part of Anhui Province. Its geographical coordinates are 116°24'30"-118°00'00" east and 30°58'40"-30°06'00" north. Including Hefei, Chaohu, Lu 'an and other 13 cities and districts. With the rapid social and economic development of Chaohu Basin, the water environment problem of Chaohu Lake has gradually worsened, becoming the main obstacle to the healthy economic, social and environmental development of the region [1]. Chaohu Lake is an important lake in the control of "three lakes" during the period of "Ninth Five-Year Plan" to "Eleventh Five-Year Plan" in China. After years of control, the deterioration of Chaohu Lake water quality has not been fundamentally improved, and there are still a lot of nitrogen and phosphorus nutrients in the lake. Especially in the western part of the lake, the phenomenon of "bloom" has been observed, and this phenomenon is increasing [2, 3]. At the same time, the nitrogen and phosphorus nutrients accumulated in the riverbed for many years have not been removed in time, and continue to affect the water quality of the river through internal discharge, and enter the Chaohu Lake through the rivers that flow into the lake. Therefore, it is necessary to manage the aquatic environment of the tributaries of the lake as a whole, control the pollution from the source better, and restore the aquatic ecosystem of the lake.

The sediment in the water body is an important enrichment source of nitrogen, phosphorus and other elements. It not only helps to purify the overburden water environment, but also plays a role of nourishment to some extent. It continuously releases nutrients to the upstream water body, thus exerting an important influence on eutrophication [4]. The absorption rate of nutrients such as nitrogen and phosphorus varies greatly among different organisms, so the forms of nitrogen and phosphorus in the substrate also show different biogeochemical behaviors. The concentration and distribution of various forms of nitrogen and phosphorus in the sediment contain abundant environmental geochemical information, so it is of great geochemical significance to study the form and distribution of nitrogen and phosphorus.

The study of nitrogen morphology in sediments began in the 1960s and 1970s, when keeney [5], kemp[6, 7], Elisa[8] and Delange [9] et al. studied nitrogen morphology in terrestrial and Atlantic sediments. At present, the analysis methods of nitrogen morphology in sediments mainly refer to soil nitrogen morphology [10], and nitrogen is divided into two parts, one organic nitrogen and the other inorganic nitrogen, in which organic nitrogen is the main component, accounting for 70-90% of the total nitrogen. The proportion of inorganic nitrogen is relatively small, accounting for only 10-30% of total nitrogen [11].

There are two main forms of organic nitrogen in sediments [12-14]. One is organic residue that is not completely degraded or partially degraded, and the other is humus. Humus is a kind of acidic high molecular weight organic matter with high nitrogen content. Humus is complex in composition and structure, usually containing amino acids, proteins and cyclic organic compounds. Organic nitrogen is mainly derived from phytoplankton, higher plants and bacteria, and its chemical forms mainly include NH3-N, amino acid nitrogen, nitrogen dissolved in sugars, nitrogen dissolved in acidic substances and nitrogen dissolved in non-acidic substances [11]. Inorganic nitrogen in sediments is a necessary nutrient for organisms in water bodies. It is directly absorbed by primary producers for photosynthesis and has important ecological significance for aquatic environment [15]. It is mainly composed of exchangeable nitrogen and fixed ammonium [16].

The focus of this study is the Shiguli River, one of the main rivers flowing into Chaohu Lake. Through field investigation, sampling, laboratory analysis and experiment, the different morphology, concentration and distribution characteristics of nitrogen and phosphorus in sediments were analyzed and evaluated. On this basis, by studying the changes of nitrogen and phosphorus nutrients in the sediment-interstitial water-soil, the migration rules of nitrogen and phosphorus nutrients in the sediment-overlying water interface of peanut were clarified. In addition, the equation of equilibrium nitrogen and phosphorus nutrient concentration in intergap water profile is proposed, which aims to provide scientific basis for restoring the water environment and analyzing the nitrogen and phosphorus load of the lake.

2. Sample Collection and Processing

2.1 Overview of the Study Area

The southern foot of Dashu Mountain in the western suburbs of Hefei is the birthplace of the fifteen mile Long River. Fifteen miles long river 28.8 kilometers, from the northwest to the southeast through Shushan, Feixi, Yandun, Changqing, Luogang, Yicheng, Dawei six cities, and finally in the city of Yicheng Tongxin Bridge into Chaohu Lake. The water level of the river is 5-7 meters wide, with a total area of 111.25 square kilometers (excluding 23.5 square kilometers of the East Levee Left Joint Protection area). Among them, the mountain area is 97.06 square kilometers, and the river bed area is 14.19 square kilometers. As one of the main flood discharge channels in the southwest of Hefei city, the Shiguli River has gradually become a polluted river in the southwest of Hefei city due to poor management and imperfect urban drainage network. The basin includes Hefei High-tech Development Zone, Political and Cultural New Area, Wanghu City, Luogang Airport and

Baohe Industrial Park. The upper reaches of the 15 Li River are mainly urban and industrial land, and the middle and lower reaches are mainly agricultural land, mainly rape and rice. Before 2000, there were large industrial enterprises such as Hefei Hongsifang Chemical Group (former Hefei Fertilizer Plant) and Jianghuai Fertilizer Plant in the basin, producing urea, fertilizer, ammonium bicarbonate, ammonium phosphate and other fertilizers and pesticides. Due to inadequate monitoring and management, a large amount of untreated and seriously polluted industrial wastewater and a small amount of domestic wastewater were directly discharged into the Fifteen Mile River, seriously deteriorating the water quality and ecological environment of the river. As a result, the water quality and ecological environment of the river have seriously deteriorated. The river is also one of the main sources of eutrophic nitrogen and potassium in the western Chaohu Lake. In 2008, Mr. Wang and his colleagues conducted monthly water quality monitoring of several Chaohu tributaries, including the Shiwuli River. The monitoring results showed that the water quality of Shiwuli River was lower than Class V throughout the year, and the average concentration was TN 22.29 mg/L, NH4+-N 19.89mg/L, TP 1.33mg/L and CODCr 32.0mg/L.

2.2 Sample Collection

(1) Layout of sampling points

After the completion of the upstream river dredging and river function improvement project, the author began to investigate the sediment pollution of the downstream river from Swan Lake to the estuary in 2009. Taking into account the specific conditions of river sections and the characteristics of runoff distribution, 15 sampling points (S1-S15) were identified in the middle of the upper and lower rivers. S1 is located at the outlet of Hefei Hongsifang Chemical Fertilizer Plant, S15 is located at the inlet of the lake, and the remaining sampling points are distributed in the industrial, urban and agricultural wastewater areas below the outlet of the ditch.

The growth of water peanut is very vigorous, and it is also the most important aquatic plant species in the river. In order to analyze the effects of aquatic peanut growth on the basic characteristics of sediment and interstitial water, three sampling points (P1, P2 and P3) were selected for the aquatic peanut growth area along the waterfront in the middle and lower reaches of the Shiguli River where aquatic peanut growth was flourishing, and a blank control point (P4) was selected in the area without aquatic plants. Among them, P1 is downstream of the sewage outlet of duck farm, P2 is near the living area of residents, and there are a lot of farmland on both sides of P3 river, and rice is the main crop, and the blank point P4 is relatively close to P1 point. These sampling sites were selected to analyze the relationship between water body growth and sedimentation, as well as the main characteristics of the intermediate water body.

(2) Sample collection and processing

In this study, sediment and pore water sampling was divided into two main phases:

In the first phase, conducted in April and May 2009, the team used specially designed sediment sampling columns to collect sediment samples at the sampling sites shown in Figure 2.1. According to the depth of sediment available for sampling, samples were taken at a depth of 50-60 cm, and local segmentation in units of 10 cm, a total of 85 sediment samples were obtained. The samples are packed in polyethylene bags, sealed and labeled on site, and immediately shipped to the lab.

In the lab, samples are kept in a cool, ventilated room and allowed to air dry. After drying, the sample is slowly split with a stick to remove debris and plant debris. The sample is then crushed, placed on a 100-mesh nylon sieve, packed in a dry storage bag, labeled, and stored in a dry environment until measured. The collection of the above samples was mainly done by other members of the research team, while the author was responsible for crushing and screening the samples.

The second phase took place between August and October 2011. At this stage, the author and other members of the research team used a self-made sediment column sampler to take four sediment samples at pre-determined sampling points in both the tussah planting area and the blank control area. The 2cm thick cylindrical sample is divided into 20 layers, a total of 80 layers. The samples are packed into ziploc bags, placed in special sealed boxes filled with ice, and rushed to a laboratory for analysis.

In the lab, each sample is further divided into two parts. The wet part is used to determine bulk density and porosity, and to obtain intermediate water; The second wet part is used to determine the form and content of nitrogen and phosphorus in the sediment after natural drying. To avoid decomposition of nitrogen and phosphorus in wet samples, the first measurements were made within 24 hours.

3. Nitrogen and Phosphorus Morphology and Spatial Distribution Characteristics of Sediments in Shiwuli River

3.1 Morphological Distribution of Nitrogen and Phosphorus in Sediments

Table 1: Nitrogen content of different sediments at different deposition depths

profundity/cm	index	SP1	SP2	SP3	SP4	SP5	SP6	SP7
0~10	TN	2717.19	261.67	21.87	1988.55	1432.25	322.26	2567.53
	NH_4^+-N	51.82	129.61	18.95	213.27	88.81	568.85	43.65
	NO_3^--N	20.34	7.73	6.56	6.15	13.18	116.41	23.62
	ON	2645.79	1924.33	1895.35	1769.12	133.24	2516.99	25.24
10~20	TN	1899.3	22.83	1652.84	1992.55	1118.68	2138.71	1798.95
	NH_4^+-N	5.68	139.96	14.73	382.21	289.45	248.52	27.33
	NO_3^--N	15.35	7.87	5.715	5.11	11.81	19.93	19.36
	ON	1832.99	1873.83	1542.48	165.41	817.41	178.75	1751.31
20~30	TN	175.87	196.14	16.5	1141.59	1323.31	156.37	213.87
	NH_4^+-N	71.49	88.12	69.96	68.66	200.07	36.21	118.42
	NO_3^--N	14.55	5.11	2.751	5.376	11.22	13.33	12.53
	ON	1664.88	1866.9	933.29	155.55	1112.23	1366.82	1972.12
30~40	TN	1594.32	1141.56	137.13	116.48	1259.68	1566.94	1181.55
	NH_4^+-N	16.25	99.97	118.83	82.18	204.46	48.9	47.355
	NO_3^--N	8.86	5.715	3.21	4.65	1.485	14.85	7.27
	ON	1569.22	135.9	1185.82	173.64	145.18	1414.56	1126.41
40~50	TN	1229.26	1454.4	1472.37	144.97	1354.53	1526.36	1549.19
	NH_4^+-N	46.25	137.6	142.18	86.67	206.56	58.56	64.43
	NO_3^--N	7.33	4.5	2.28	3.73	12.75	88.17	5.37
	ON	1175.67	1312.39	1327.93	954.49	1135.95	1379.67	1479.37
50~60	TN	1432.2	1219.36	-	1298.88	1216.34	1193.26	1412.88
	NH_4^+-N	117.73	159.58	-	229.48	255.475	394.62	265.77
	NO_3^--N	3.92	3.33	-	2.68	7.87	81.76	4.12
	ON	131.55	156.45	-	166.75	953.77	716.87	1142.87

In order to study the morphological distribution of nitrogen and phosphorus in sediments, 7 representative points were selected from 15 sampling points (such as S1, S2, *d*, S15, etc.) for analysis to make them more recognizable and labeled as SP1, SP2, d, and SP7 respectively. Specifically, SP1 corresponds to S1 and SP2 corresponds to S3. SP3 corresponds to S5 points, SP4 corresponds to S7 points, SP5 corresponds to S8 points, SP6 corresponds to S10 points, SP7 corresponds to S12 points, etc. According to the experimental method, the concentrations (mg/kg) of nitrogen forms in sediments at these sampling sites and the corresponding results are shown in

Table 1.

Table 2: Phosphorus content of different forms at different deposition depths

profundity/cm	index	SP1	SP2	SP3	SP4	SP5	SP6	SP7
0~10	TP	1047.01	64.61	94.11	98.22	60.02	1570.11	866.74
	Ex-P	26.87	22.26	38.07	1.37	24.47	38.28	41.27
	Al-P	5.19	6.00	3.58	6.80	6.00	3.58	1.73
	Fe-P	613.42	187.49	344.61	417.26	375.48	720.51	251.37
	Oc-P	26.87	27.69	39.17	39.73	36.51	38.14	30.85
	Ca-P	40.58	35.14	380.60	404.58	10.13	343.48	333.17
	De-P	81.47	27.69	23.64	41.34	40.52	26.08	34.85
	OP	92.16	36.53	39.68	67.10	19.65	18.86	4.94
10~20	TP	699.12	699.86	750.93	920.33	674.66	1416.00	74.68
	Ex-P	8.40	16.44	27.68	8.40	14.83	266.96	34.05
	Al-P	1.97	3.59	1.18	1.18	5.19	1.97	1.98
	Fe-P	51.17	208.36	362.99	51.02	312.11	681.35	202.13
	Oc-P	19.65	20.45	2.35	33.29	34.09	30.89	22.83
	Ca-P	41.33	360.45	256.53	331.24	170.60	38.38	337.18
	De-P	85.49	25.94	22.44	5.11	57.38	18.84	56.51
	OP	81.47	29.30	34.09	57.36	4.14	20.44	41.27
20~30	TP	589.64	56.18	80.40	16.21	541.12	116.91	6.01
	Ex-P	5.20	17.23	37.31	6.79	12.42	118.37	14.01
	Al-P	1.18	3.58	1.18	0.37	1.98	0.37	1.18
	Fe-P	443.77	125.64	173.82	310.01	271.36	397.01	187.28
	Oc-P	18.05	30.08	27.68	23.64	4.16	30.07	10.00
	Ca-P	33.31	298.47	44.74	58.28	133.72	506.89	253.16
	De-P	59.82	8.40	27.68	5.36	49.56	36.50	14.01
	OP	36.52	2.35	30.08	54.12	18.85	46.94	12.40
30~40	TP	368.75	524.43	584.57	731.40	488.67	193.94	718.38
	Ex-P	6.00	12.29	17.23	6.00	14.03	117.71	39.70
	Al-P	1.18	1.98	0.37	5.19	2.78	1.18	1.18
	Fe-P	160.22	128.10	60.60	31.32	186.67	395.44	206.67
	Oc-P	13.23	16.44	37.31	3.33	18.84	26.87	20.44
	Ca-P	3.35	300.28	397.85	351.32	158.66	507.85	332.69
	De-P	140.94	7.60	25.83	30.88	44.54	38.12	40.51
	OP	4.16	48.57	13.22	45.33	23.66	50.96	39.48
40~50	TP	382.34	490.19	492.86	48.83	397.58	1254.86	695.54
	Ex-P	2.78	13.23	28.48	4.39	7.60	144.06	3.31
	Al-P	2.78	1.18	1.18	4.39	3.59	1.18	0.37
	Fe-P	157.01	145.53	61.40	98.33	130.50	403.34	183.27
	Oc-P	20.45	18.85	26.88	36.51	29.30	3.33	37.28
	Ca-P	30.90	230.94	39.06	23.92	123.27	542.21	34.55
	De-P	140.14	19.66	26.07	14.03	43.75	33.29	46.10
	OP	55.00	59.82	16.43	34.09	25.94	5.78	30.86
50~60	TP	811.46	438.59	-	652.35	385.32	1326.45	773.05
	Ex-P	3.40	8.40	-	5.20	10.01	160.17	35.67
	Al-P	1.97	0.37	-	2.78	1.18	0.37	0.37
	Fe-P	591.51	138.50	-	124.11	142.57	381.54	188.90
	Oc-P	12.18	9.21	-	30.90	2.35	22.86	26.04
	Ca-P	61.40	224.10	-	395.16	116.80	629.11	374.99
	De-P	14.03	1.37	-	26.08	39.48	47.74	88.61
	OP	65.42	43.73	-	36.53	30.08	73.45	29.30

In order to determine the distribution of phosphorus in sediments, the chemical continuous extraction method was used to analyze the phosphorus in each sedimentary layer in detail. The corresponding concentration measurements (mg/kg) are summarized in Table 2 for comparison.

3.2 Nitrogen Content of Different Forms

Different forms of nitrogen in sediments include organic nitrogen and inorganic nitrogen, and total nitrogen is the sum of organic nitrogen and inorganic nitrogen. We analyzed different sampling points (SP1, SP2,...) at different deposition depths in the 15 Li River. SP7), the concentration of different forms of nitrogen, and the results are summarized in Table 3. The data showed that nitrogen pollution in the sediments was quite a problem, with TN at different depths ranging from 1,295.48 mg/kg to 2,282.91 mg/kg. The average organic nitrogen content at different depths ranged from 1041.21mg/kg to 2083.17mg/kg, and the proportion of TN content ranged from 60.1% to 98.4%. In contrast, the average concentration of exchangeable inorganic nitrogen (i.e., NH4+-N and NO3--N) is 88.16-237.11 mg/kg and 17.16-27.71 mg/kg, respectively, accounting for only 1.02% to 33.07% and 0.16% to 6.86% of TN, which is significantly lower than the organic nitrogen content. This suggests the dominance of organic nitrogen in the sediments of the Fifteen Five-Li River, a trend similar to that of many lakes, bays, and other large bodies of water. It is worth noting that at each sampling point, the average concentration of NH4+-N at the same deposition depth is significantly higher than NO3--N. In general, the concentration of NH4+-N in the sediments of the Shilihe River decreases first and then increases with the increase of deposition depth, while the concentration of NO3--N slightly decreases, but the amplitude changes are relatively stable. According to the analysis of the change amplitude of the standard deviation relative to the mean value, it can be seen that NO3--N is the most uneven, followed by NH4+-N, while the distribution of total nitrogen and organic nitrogen is relatively uniform.

Table 3: Statistical results of nitrogen content in different forms

profundity /cm	Project	index(mg/kg)				
		TN	NH_4^+-N	NO_3^--N	DIN	ON
0~10	Average value	2282.91	172.04	27.71	199.77	2083.17
	Standard deviation	584.25	183.93	39.71	220.19	483.87
10~20	Average value	1802.97	176.57	24.91	202.37	1600.6
	Standard deviation	340.64	133.3	37.85	142.86	365.3
20~30	Average value	1541.63	94.99	22.12	117.12	1424.51
	Standard deviation	414.33	52.41	36.08	48.37	414.69
30~40	Average value	1315.89	88.16	20.65	108.81	1207.09
	Standard deviation	189.97	62.02	37.18	62.87	205.86
40~50	Average value	1375.82	106.04	17.57	123.61	1252.21
	Standard deviation	182.4	58.23	31.3	56.6	175.71
50~60	Average value	1295.49	237.11	17.16	254.27	1041.21
	Standard deviation	104.86	96.21	31.69	123.34	198.3

3.3 Content of Different Forms of Phosphorus

The presence of phosphorus in sediments can generally be divided into two categories: inorganic phosphorus and organic phosphorus. Inorganic phosphorus includes exchangeable phosphorus (Ex-P), aluminium-bound phosphorus (Al-P), iron-bound phosphorus (Fe-P), closed storage phosphorus (Oc-P), authigenic phosphorus (Ca-P) and detritus phosphorus (De-P). Due to the difference of sedimentary environment, hydrodynamic conditions and man-made pollution, the concentration of total phosphorus and different forms of phosphorus in different reaches of the river is also different. The results are shown in Table 4. The table shows that the average total phosphorus

(TP) concentration at different depths ranges from 591.39 mg/kg to 942.57mg/kg. Among the different forms of phosphorus, the highest average concentration is iron-bound phosphorus (Fe-P), which ranges from 168.4mg/kg to 415.68mg/kg, followed by autogenous phosphorus (Ca-P), which ranges from 257.08mg/kg to 318.03mg/kg. The content of the other five kinds of phosphorus is much lower than that of Fe-bound phosphorus and authigenic phosphorus, indicating that Fe-bound phosphorus and authigenic phosphorus are the main total phosphorus components in the sediments. This trend is consistent with the distribution pattern of phosphorus in Chaohu estuary and sediment. In general, the contents of exchangable phosphorus (Ex-P), closed storage phosphorus (Oc-P), detrital phosphorus (De-P) and organophosphorus (Or-P) are close, while the content of aluminum-bound phosphorus (Al-P) is the lowest, with an average of 1.18 mg/kg to 4.69mg/kg, accounting for only 0.03% to 1.03% of total phosphorus. Reactive phosphorus such as exchangeable phosphorus and aluminum-bound phosphorus are slightly higher in the upper layer of sediments (0-20 cm), with little variation or difference in concentration between layers. In contrast, inactive phosphorus (such as closed storage phosphorus, detritus phosphorus and organophosphorus) did not change significantly with sediment depth. In conclusion, the proportion of different phosphorus concentrations in total phosphorus in the sediments of Shiwuli River is as follows: Fe-bound phosphorus ≈ autogenetic phosphorus > exchangeable phosphorus > detrite phosphorus > Organophosphorus > closed storage phosphorus > Al-bound phosphorus.

Table 4: Statistical results of phosphorus content in different forms

profundity /cm	Project	index(mg/kg)							
		TP	Ex-P	Al-P	Fe-P	Oc-P	Ca-P	De-P	Or-P
0~10	Average value	942.57	69.33	4.69	415.68	34.09	277.8	39.36	45.02
	Standard deviation	322.89	111.78	1.8	190.47	5.49	146.31	19.82	26.18
10~20	Average value	842.37	60.32	2.44	374.73	26.06	267.99	44.12	42.35
	Standard deviation	265.72	101.76	1.46	163.86	6.41	122.85	24.18	20.71
20~30	Average value	739.5	30.19	1.41	272.69	24.57	318.03	35.47	31.45
	Standard deviation	265.44	40.3	1.11	118.87	8.05	197.43	19.71	15.31
30~40	Average value	665.58	30.31	1.97	194	23.54	297.18	46.84	36.16
	Standard deviation	284.87	40.16	1.61	103.9	8.72	157.28	43.27	13.91
40~50	Average value	591.39	33.17	2.09	168.4	28.71	257.08	46.15	39.14
	Standard deviation	310.78	50.21	1.5	110.97	7.21	163.13	43.09	16.64
50~60	Average value	731.1	37.14	1.18	261.19	20.32	300.26	58.17	46.27
	Standard deviation	338.93	61.41	1.02	188.01	8.38	209.4	46.63	18.9

4. Longitudinal Distribution Characteristics of Nitrogen and Phosphorus Forms in Sediments

4.1 Longitudinal Distribution Characteristics of Nitrogen Morphology

At the sediment-water interface, NH4+-N and NO3--N are mainly transported and released in exchangeable nitrogen forms, and participate in the biogeochemical nitrogen cycle. We investigated the nitrogen forms at different deposition depths in the Shiguli River, and the specific data are shown in Table 5. According to the data in the table, the following longitudinal distribution characteristics of nitrogen morphology can be obtained:

For NH4+-N, the concentration of SP6 was the highest at 0-10 cm deposition depth (568.85mg/kg), followed by SP4 (213.27mg/kg), SP1 (51.82mg/kg) and SP7 (43.65mg/kg). The concentration of SP4, SP5 and SP6 was significantly higher than that of other sample points in the range of 10-20 cm, among which the concentration of SP4 reached the highest value (382.21mg/kg), while the concentration of SP7 was the lowest (27.33mg/kg). Between 20 and 30 cm, SP5 had the highest concentration (200.07mg/kg), followed by SP7 (118.42mg/kg), and SP6 had the lowest concentration (36.21mg/kg). At the depth of 30-40 cm, the concentration of SP5 was the highest (204.46mg/kg), followed by SP3 (118.83mg/kg) and minimum SP1 (16.25mg/kg). At the depth of 40-50 cm, the concentration of SP5 was the highest (206.56mg/kg), followed by SP3 and SP2 (142.18mg/kg and 137.6mg/kg, respectively), and other sampling points were relatively close.

At the deposition depth of 50-60 cm, SP6 had the highest concentration (394.62 mg/kg), followed by SP7, SP5 and SP4, while SP1 had the lowest concentration (117.73 mg/kg). In the range of 0-10 cm deposition depth, the NO3--N concentration of SP6 was the highest (116.41 mg/kg), which was several times that of other sampling points, followed by SP7 and SP1 (23.62 mg/kg and 20.34 mg/kg, respectively), with little difference among other sampling points. The concentration of NO3--N between 10 and 20 cm showed a similar trend, but between 20 and 60 cm, the concentration of NO3--N in SP6 was the highest, higher than that in other sampling points, and there was little difference in the other points.

In the range of 0-10 cm depth, the maximum value of organic nitrogen was 2645.84mg/kg (at SP1), followed by 2517mg/kg (at SP6), 2500.25mg/kg (at SP7), and the lowest value was 1330.25mg/kg (at SP5). In the range of 10 to 20 cm depth, the concentration of organic nitrogen was not different at all points except SP5, which was significantly lower. In the other depth range, the organic nitrogen concentration at each point has little change and is basically stable.

As for TN, the TN content of SP6 is unusually high at the deposition depth of 0-10 cm, reaching 3202.27 mg/kg, followed by 2717.26 mg/kg of SP1 and 2567.53 mg/kg of SP7, while the content of SP5 is the least. It was 1432.25mg/kg. At depths of 10 to 20 cm, the changes at each point are the same as in the surface layer, while in the other layers, the changes in TN content are basically the same as the changes in organic nitrogen.

In general, the nitrogen content of different forms in SP4, SP5 and SP6 samples was higher, especially in the range of 0 to 20 cm depth. This may be related to the exposure of these sites to more complex environmental pollution. For example, SP4 is located near the discharge of domestic sewage in the village, SP5 is located near a fish pond not far upstream, and SP6 is located in an area with more complex environmental pollution, about 20 to 30 meters upstream, there is a poultry farm, and many crops (mainly rice) are grown on the banks of the river. Large amounts of poultry manure and pesticide waste with high levels of nitrogen and phosphorus flowed into the river, resulting in high nitrogen concentrations in the sediments at the three sites.

4.2 Longitudinal Distribution Characteristics of Phosphorus Form

The Ex-P concentration at each sampling point varies greatly in different deposition depths.

Among them, the concentration of SP6 reached a peak of 321.78mg/kg near the surface of 0 to 10 cm, which was much higher than the concentration of other sites. The concentration of SP1 near the surface was the lowest (2.78mg/kg). SP7 and SP3 sampling points have little difference in each layer, and the concentration is relatively higher than that of other sampling points, while the content of other sampling points is relatively close. In contrast, SP2 and SP5 are slightly higher than SP2 and SP4.

The content of Al-P in the form of phosphorus is the lowest in the sediments of Shiwuli River, and it changes with the sediment depth, but the value difference is not significant. In general, the vertical distribution of Al-P in the fifteen mile River is not obvious. The Fe-P content of SP6 was 639.3 mg/kg in 0-10 cm sediments, followed by SP1 and SP4, 613.42 mg/kg and 417.26 mg/kg, respectively. The lowest was 187.49 mg/kg of SP2, which was similar in the other 4 sites. The content distribution at 10~20 cm was similar to that at 0~10 cm overlying soil layer. At 20~30 cm, the content of SP1 was the highest (443.77 mg/kg), followed by SP6 (396.91 mg/kg) and SP2 (125.64 mg/kg), while the content of SP4 and SP5, SP3 and SP7 were close to each other. From 30 to 40cm, except for SP6 (395.44mg/kg), SP4 (220.32mg/kg) is second only to SP6, and the smallest is SP3 (60.6mg/kg), other sampling points are relatively close. At 40~50 cm, the maximum and minimum values are still SP6 and SP3, which are 403.34 mg/kg and 61.4 mg/kg, respectively, and there is no significant difference among other sampling points. In the bottom 50~60 cm, the maximum content of SP1 was 591.51 mg/kg, SP6 (381.54 mg/kg) was second only to SP1, and there was no significant difference among other sampling points. In general, the highest Fe-P content was concentrated in SP6, and the content of S1 and S4 was also higher, second only to SP6.

The concentration of Oc-P varies slightly with sediment depth, but the overall change is not obvious.

For Ca-P, the maximum and minimum values appear at SP6 and SP1, respectively, in each deposition depth, while the other sites do not change much with the deposition depth.

For De-P, the maximum of SP1 appears at different deposition depths, and the concentration of SP1 is significantly higher in all layers than at other sampling points, while the concentration of other sampling points is similar at all deposition depths.

For Or-P, at the depth of 0~20 cm, the maximum value appears at SP1, followed by SP4, and the minimum value at SP6, while the concentration of other sampling points is similar. At the depth of 20-30 cm, the maximum value appeared in SP4 (54.12 mg/kg), followed by SP6 (46.94 mg/kg), and the minimum value appeared in SP7 (12.4 mg/kg). At 30-50 cm depth, except for the lowest concentration of SP3, there is no significant difference between the concentration values at 30 to 50 cm depth at other sites. At the depth of 50-60 cm, SP6 points had the highest concentration of 73.45 mg/kg, followed by 65.42 mg/kg at SP1 points, and the other sampling points had little difference.

In all sediment depths of SP6 sampling sites, TP concentration is very high, while in other sampling sites, TP concentration is high only in individual sediment depths, but the overall difference is not significant. The significant changes in the vertical distribution of phosphorus form in the above sediments may be related to the introduction of external AIDS.

5. Vertical Distribution Characteristics of Nitrogen and Phosphorus Forms in Sediments

5.1 Vertical Distribution Characteristics of Nitrogen Morphology

As far as TN is concerned, except for SP5, the content of all other sampling points gradually decreases with the increase of deposition depth. Among them, SP3, SP4, SP6 and SP7 decrease significantly at 0-30 cm depth and then basically stabilize. SP2 barely changed at 0-30 cm depth, but decreased significantly at 30-40 cm depth. In terms of NH4+-N, the concentration of SP1, SP2, SP3, SP5 and SP7 gradually increases with the increase of depth, but in SP4 and SP6, the concentration gradually increases after different degrees of reduction, and sharply decreases within the depth range of 20~30 cm. The soil layer in the depth range of 50 to 60 cm increased dramatically. On the contrary, at all sampling points, NO3--N concentration gradually decreased with increasing depth, which was consistent with the general characteristics of aquatic sediments. The distribution of these different forms of nitrogen is affected by the REDOX environment. NH4+-N exists mainly in the adsorbed form of negatively charged substances in sediments, mostly in the form of exchangeable ions, and partially dissolved in intermediate water. The NH4+-N content increases with depth because the reduction conditions promote the retention of ammonium nitrogen in the sediment. The decreasing trend of NO3--N content with increasing depth is mainly due to the fact that NH4+-N is converted to NO3--N through nitrification in the near surface oxidation layer with the participation of ammonium oxidation and nitrite-oxidizing bacteria, resulting in rich nitrate nitrogen in the near surface layer. Under hypoxic conditions, NO3--N becomes an alternative electron acceptor for anaerobic bacteria, and denitrification occurs, and NO3--N is transformed into NH4+-N and NO2--N. Therefore, NO3--N decreased and decreased with the increase of deposition depth. The variation trend of ON concentration was consistent with that of NO3--N concentration, and all sampling points showed a decreasing trend with increasing depth, but the reduction of SP1, SP6 and SP7 was significantly greater than that of other sampling points.

5.2 Vertical Distribution Characteristics of Phosphorus Form

The vertical distribution pattern of phosphorus is often complicated and depends on the interaction of various influencing factors such as river ecological conditions, pollutant emission intensity and sedimentary environment.

In general, the concentrations of Ex-P, Al-P, Fe-P and Or-P tend to decrease as the sediment depth increases. On the other hand, Oc-P, Ca-P, and De-P do not follow a pattern in the vertical direction, but there are some variations. The details are as follows:

The surface layer (0~10 cm) of each sampling point had higher Ex-P concentration, especially SP6. However, as the depth increases, the Ex-P concentration gradually decreases. During the field investigation, a large number of aquatic plants (mainly water peanuts) were observed growing in the Fifteen Mile River. These aquatic plants promoted soil activation and increased Ex-P content. It can be considered that aquatic vegetation has a greater influence on the vertical distribution of Ex-P in the sediments of the 15 Li River. Ex-P, the most active form of phosphorus in sediments, is directly absorbed and used by zooplankton in upstream streams, contributing to the formation of blooms. However, the amount of Ex-P in the sediment is not large, so its release has less impact on the water body.

In general, the concentration of Al-P decreased with increasing depth. The distribution of Al-P in the sediments in the Weishan area of Nansi Lake shows an increasing trend with the increase of depth, while the distribution of Al-P in the sediments of Wulianghai shows an increasing trend with the increase of depth and then a decreasing trend. Therefore, the distribution of Al-P in sediments and its migration mechanism need to be further studied in detail.

In this study, the vertical distribution of Fe-P content fluctuated and decreased at each sampling point. This may be due to the increase of dissolved oxygen consumption due to the decomposition of organic matter with the increase of deposition depth, which leads to the relative reduction of sedimentary environment and the decrease of REDOX potential. With the reduction of Fe3+ to Fe2+, Fe-P is gradually released into the pore water, and then gradually migrates upward through the overlying water through the concentration gradient, resulting in the formation of mineral precipitation with high reoxidation potential in the surface sediments, resulting in Fe-P enrichment.

In addition, with the increase of deposition depth, amorphous minerals gradually order, weaken the ability of iron oxides and hydroxides to combine with phosphorus, which is also the reason for the reduction of iron-phosphorus content.

The vertical variation characteristics of Oc-P at each sampling point are relatively small, but SP3, SP4 and SP7 show fluctuating variation characteristics, with the content dropping sharply in the depth range of 0~30 cm, rising sharply in the depth range of 30~50 cm, and then falling again at the bottom of these sampling points. This may be related to the weak ability of Oc-P to participate in the biogeochemical cycle of phosphorus.

In contrast, the vertical distribution of Ca-P in sediments is relatively complex. Ca-P increases gradually with the increase of depth at all sampling sites except SP2, and the increase of SP6 is significantly greater than that at other sampling sites. In the depth range of 20~40 cm, SP3 and SP4 generally show an upward trend, but there are also some vertical fluctuations. This may be due to Ca-P produced by organophosphorus (OP) conversion. Dissolved phosphorus released by OP adsorbed on iron oxides to form phosphorus-iron complexes, which were gradually deposited and buried in sediments. In the reducing environment, the iron (OOH) in the phosphate-iron complex gradually dissolves and migrates to the upper sediments, while in the lower anoxic environment, the iron-released phosphorus particles gradually mineralize and eventually form Ca-P. Because the lower sediments experience longer than the upper sediments, the content of Ca-P gradually increases with the depth of deposition.

There were significant differences in the vertical distribution characteristics of De-P concentration at different sampling points. In SP1 and SP7, De-P concentration showed an oscillatory upward trend with the increase of deposition depth, and then gradually decreased, with the lowest value appearing at 30 cm. On the other hand, SP2, SP3 and SP5 show a basically stable trend, but also fluctuate with the change of deposition depth. In addition, the variation amplitude of SP4 has decreased. In general, there was a vertical variation in De-P content at each sampling site, but the degree of variation was limited. This may be due to the fact that De-P is formed primarily by authigenic and biological factors as well as phosphorus precipitated from authigenic calcium carbonate. Because these components are relatively stable in nature, there is limited variation in their vertical distribution.

Or-P is mainly composed of organic matter, including the remains of various plants and animalsInositol hexaphosphate and humus. These organic substances are only released when the organic matter is mineralized. At all sampling sites except SP5 and SP6, the Or-P content gradually decreased with increasing deposition depth. This may be due to increased anaerobic action with increasing deposition depth, which promotes mineralization of organic matter and conversion of Or-P to other bioavailable forms of phosphorus. In this regard, Rydin's research results on the sediments of Lake Erken in Sweden also show that the Or-P content gradually decreases with the increase of sediment depth, which is consistent with our experimental results.

6. Correlation Analysis of Sediment Nitrogen and Phosphorus

There is clearly a certain correlation between different forms of nitrogen and phosphorus in the sediments of the Shiguli River. TN is positively correlated with TP, Fe-P and Ex-P, and the correlation coefficients are 0.471, 0.438 and 0.566, respectively. The correlation coefficients between NH4+-N and Fe-P (R=0.309) and TP (R=0.354) are also very significant. There was a highly significant correlation with Ex-P (R=0.479). On the other hand, NO3--N was positively correlated with Ex-P, Fe-P, Ca-P and TP, and the correlation coefficients were 0.909, 0.607, 0.438 and 0.798, respectively. There was a significant positive correlation between ON and Fe-P (R=0.469). The significant correlation between various forms of nitrogen and Fe-P and Ex-P indicates that the two are closely related. However, Al-P, Oc-P, De-P and Or-P had low correlation with their respective forms of nitrogen. This suggests that the four types of phosphorus are weakly related to nitrogen release, and may even be completely different processes. TN was highly correlated with ON (R=0.964), but there was no significant correlation between different nitrogen forms. In particular, no clear correlation was observed between NH4+-N and NO3--N, suggesting a difference between the two sources. A weak negative correlation was also observed between NH4+-N and ON, indicating that it is unlikely that ON will convert to NH4+-N. The correlation between NH4+-N and ON is not obvious. The reason for this may be insufficient hydrodynamic conditions in the river channel. Under the condition of sufficient dissolved oxygen, microorganisms cannot convert ON into NH4+-N and NO3--N through ammonification or nitrification.

There is a good correlation between TP content in sediments and Ex-P, Fe-P, Oc-P, Ca-P and Or-P, which is consistent with the study results of Xiangsulin in the sediments of Poyang Lake. In different forms of phosphorus, there was a very significant positive correlation between Ex-P and Fe-P and Ca-P, and the correlation coefficients were 0.617 and 0.43, respectively, indicating that part of Ex-P might come from the transformation of Fe-P and Ca-P. The correlation coefficient between Al-P and Oc-P was 0.417, and between Ca-P and De-P was 0.491, indicating that there is a transformation relationship between these phosphorus, that is, phosphorus that is difficult to release into the water body may be converted into more easily released phosphorus under certain conditions. Ca-P and De-P are negatively correlated (R =-0.491), indicating that there is an internal relationship between them. Similarly, the correlation coefficients between De-P and Or-P and Oc-P and Ca-P are 0.374 and 0.335, respectively, which also reflect the transformational nature of this source property.

Table 5: Correlation coefficients of different forms of nitrogen and phosphorus

Project	TN	NH_4^+-N	NO_3^--N	ON	Ex-P	Al-P	Fe-P	Oc-P	Ca-P	De-P	OP	TP
TN	1											
NH_4^+-N	0.222	1										
NO_3^--N	0.338*	0.286	1									
ON	0.964**	-0.038	0.208	1								
Ex-P	0.438**	0.479**	0.909**	0.272	1							
Al-P	0.255	0.076	-0.152	0.258	-0.106	1						
Fe-P	0.566**	0.309*	0.607**	0.469**	0.617**	0.15	1					
Oc-P	0.192	0.246	0.202	0.125	0.275	0.417**	0.161					
Ca-P	-0.036	0.156	0.438**	-0.109	0.43**	0.243	0.012	0.335*	1			
OP	0.071	-0.145	0.065	0.106	-0.087	0.055	0.374*	-0.174	0.005	0.371*	1	
TP	0.471**	0.354*	0.798**	0.345*	0.814**	-0.046	0.78**	0.356*	0.602**	-0.105	0.291*	1

7. Discussion

In aquatic environments, nitrogen and phosphorus are present in sediments in different forms and play different roles. Bioavailable nitrogen (NH4+-N, NO3--N) and bioavailable phosphorus (Ex-P, Al-P, Fe-P) are important components in sediments, which can be directly utilized by organisms. They play an important role in the geochemical cycles of nitrogen and phosphorus. Surprisingly, forms of nitrogen and phosphorus that are not directly used by organisms can also be converted into biologically active phosphorus under certain conditions, thus promoting the nitrogen and phosphorus geochemical cycle. For example, ON is not active in the biochemical nitrogen cycle, but will gradually degrade to simple organic amino compounds through amination under the synergistic action of the sedimentary environment and microorganisms. Most of the nitrogen released during ammonification combined with organic and inorganic acids to form ammonium salts, which were absorbed by plants or further oxidized to nitrates through nitration. In the river sediments of 15 Li, the inorganic nitrogen in exchangable form NH4+-N and NO3--N accounted for

1.6%-33.1% and 0.16%-6.9%, respectively. It shows that ON is the main source of sediment pollution. The data in the table show that the amount of inorganic phosphorus exceeds the total phosphorus by absolute advantage, indicating that the total phosphorus is mainly inorganic phosphorus. Considering the land use situation, pollution source distribution and sewage discharge in the basin area, it can be preliminatively concluded that the organic nitrogen wastewater and urban domestic sewage discharge from the former Sifang fertilizer plant in the upper reaches, the excessive use of fertilizers (mainly nitrogen and phosphorus) in the middle and lower reaches of farmland, the use of pesticides and the runoff from fish farms, etc., are the main sources of nitrogen and phosphorus in the sediments of the Shiwuli River, and the main causes of pollution. This helps explain the complex relationship between different forms of nitrogen and phosphorus. At sampling point SP6, concentrations of NH4+-N, NO3--N, Ex-P, and Fe-P are many, many times higher than at other sampling points in the same depth range. Investigation of the sampling sites suggests that the cause of this abnormal elevation may be several large fish ponds and open poultry farms on the upper right bank of SP6. Large amounts of fish feed and chicken manure containing nitrogen and phosphorus were discharged directly into the Fifteen Li River with rain, resulting in abnormally high concentrations of bioavailable nitrogen and phosphorus in SP6. In different deposition depths (such as 0~10 cm, 10~20 cm, 20~30 cm and 30~40 cm), Fe/Al-P accounted for 44.8%, 44.29%, 38.87% and 30.57% of TP, respectively, indicating that Fe/Al-P was mainly affected by anthropogenic pollution. In contrast, Oc-P, Ca-P, De-P and Or-P are stable and less affected by anthropogenic pollution. The analysis of these four phosphorus forms in this study also confirmed that they are mainly derived from nature, such as the geological conditions of the watershed. In 2008, the amount of TP entering Chaohu Lake from Shili River reached 146 tons, and the downstream water body, Chaohu Lake, increased the nutritional risk of the water body due to the large amount of bioavailable phosphorus in the upper sediment of the riverbed. This view is also supported by the frequent occurrence of severe "blooms" in the 15 Li estuary over the past decade. By analyzing nitrogen and phosphorus patterns and bioavailability at different sediment depths, this study provides scientific basis for determining dredging depth for river restoration and pollution control of Chaohu Lake.

8. Conclusion

(1) The nitrogen and phosphorus forms in sediments from 0~60 cm deep in the Shiwuli River were analyzed in detail. The results showed that the average TN content ranged from 1,295.48 to 2,282.91 mg/kg, of which 60.1% to 98.4% was ON, which was the main component of TN. The average contents of NH4+-N and NO3--N were 88.16-237.11 mg/kg and 17.16-27.71 mg/kg, respectively. The order of nitrogen content in different forms was ON > NH4+-N > NO3--N; The average content of TP was 591.39 ~ 942.57mg/kg. Among the different forms of phosphorus, Fe-P and Ca-P had the highest content, 168.4 ~ 415.68mg/kg and 257.08 ~ 318.03mg/kg, respectively, while the content of Al-P was the lowest. Only 1.18 to 4.69mg/kg. The order of different forms of phosphorus is as follows: Fe-P≈Ca-P > ex--P > OP > De-P > Oc-P > Al-P.

(2) The longitudinal analysis shows that in the middle and lower reaches of the river, the NH4+-N content is relatively high at sampling points SP4, SP5 and SP6, especially in the sedimentary depth range of 0~20 cm; In terms of NO3--N, the SP6 content of the sampling sites was significantly higher, but the other 6 sampling sites had little difference in content, and the overall change of nitrogen content was not obvious. The highest levels of Fe-P were concentrated in SP6, SP1, and SP4, while all other forms of phosphorus showed complex differences when vertical effects were taken into account.

(3) In the vertical direction, TN, ON and NO3--N decrease with the increase of deposition depth,

while NH4+-N increases with the increase of deposition depth. Fe-P decreased with the increase of deposition depth, and Ex-P and Al-P did not change much with the increase of deposition depth except for 0-20 cm sedimentary layer. On the other hand, Oc-P, Ca-P, De-P and Or-P do not change much with deposition depth.

(4) SPSS 18.0 software was used to conduct correlation analysis of nitrogen and phosphorus contents in sediments. The results show that there are different correlations between different forms of nitrogen and phosphorus in the sediments of the 15 Li River, and there is some homology or transformation relationship between them. However, it should be noted that there is no obvious correlation between NH4+-N and NO3--N.

(5) According to the overall distribution of land use and pollution sources in the basin, as well as the comprehensive analysis of the experimental data, it is preliminatively concluded that the main sources of nitrogen and nitrogen pollution are organic nitrogen and urban drainage in the wastewater of the former Jianghuai Fertilizer plant and Hongsifang Chemical Group in the upstream, excessive use of chemical fertilizers and pesticides in the middle and downstream farmland, and aquaculture drainage.

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