

## Spatial Distributions and Environmental Significance of Nitrogen in Sediments of Two Typical Urban Shallow Lakes in Southern Fujian, P.R. China

PEI-YONG GUO<sup>1,\*</sup>, JIN-MING WANG<sup>1</sup>, PENG-YU XU<sup>1</sup>, XIAO-YAN ZHAO<sup>1</sup> and CHEIN-CHI CHANG<sup>1,2,3</sup>

<sup>1</sup>Department of Environmental Science and Engineering, College of Chemical Engineering, Huaqiao University, Xiamen 361021, Fujian, P.R. China

<sup>2</sup>Department of Engineering and Technical Services, D.C. Water and Sewer Authority, Washington, D.C. 20032, USA

<sup>3</sup>Department of Civil and Environmental Engineering, University of Maryland, Baltimore County, Baltimore, MD 21250, USA

\*Corresponding author: Tel: +86 0595 222692065; E-mail: peiyongguo@126.com

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In this article, contents and distributions of N-forms in sediments from two typical urban shallow lakes in southern Fujian province of China were studied with the purpose of evaluation of nitrogen contamination and its risk to aquatic systems. Meanwhile, from different perspectives, relevant factors and environmental significance were also analyzed. The main results are as follows, (1) Non-transferable nitrogen (NTF-N) is the dominant form in total nitrogen; transferable nitrogen (TF-N) accounts for 17.64 and 17.20 % of total nitrogen, respectively. (2) The contents of IEF-N, WAEF-N and SOEF-N are positively correlated with total organic carbon in sediments. Also, the contents of IEF-N and SOEF-N are positively correlated with chlorophyll-a of the overlying water. (3) The four forms of TF-N, reciprocally interacted, are not obviously affected by temperature, pH and dissolved oxygen in the overlying water. Nitrogen in sediments is a good indicator of lake eutrophication, therefore, it has a very important environmental significance.

**Key Words:** Nitrogen form, Distribution, Sediment, Environmental significance, Lake.

### INTRODUCTION

Nitrogen is one of necessary nutritional elements for organisms and restrictive nutrients to its primary productivity<sup>1,2</sup>. Nitrogen in sediments exists in different physico-chemical forms with different geochemical characteristics and plays different roles in biogeochemical cycle. So, quantitative research on N-forms in sediments become an important precondition in explorations of nitrogen biogeochemical function. Currently, studies on nitrogen in lake sediments have mostly focused on total nitrogen and species, such as  $\text{NH}_4^+\text{-N}$ ,  $\text{NO}_3^-\text{-N}$ ,  $\text{NO}_2^-\text{-N}$ <sup>3-5</sup>. These parameters, however, cannot exactly indicate potential risk in eco-environment. For example,  $\text{NH}_4^+\text{-N}$  is recognized as the dominant species of inorganic nitrogen in sediment, but only a small fraction of nitrogen in this form can be released into lake water to become available for primary production<sup>6</sup>. The reason is that majority of  $\text{NH}_4^+\text{-N}$  is contained within crystal lattice of sediments and is immobile<sup>7</sup>. There are great disparities when organisms absorb and utilize different forms of nitrogen, which in sediments have different bioavailability. Therefore, when it comes to evaluation of releasing potential of nitrogen in sediments, it is much better to research N-forms than to research total nitrogen. Nitrogen contents and

distributions are also closely linked to lake eutrophication, so the contents and distributions of nutrients in the sediments can reflect whether the lake area is polluted<sup>8-10</sup>.

In China, with the rapid economic development and urban expansion, massive wastes and pollutants are poured into lakes nearby. As a result, lake eutrophication has become a serious environmental problem, especially for shallow lakes in the cities like Quanzhou city, Southern Fujian province, China. In the past few years, some scholars have studied the distribution and transportation mechanisms of nutrients in the East Lake and West Lake of Quanzhou city and obtained the characteristics of their distributions in overlying water and their transportation mechanisms<sup>11-13</sup>. In addition, the characteristics of sediments and overlying water quality will affect the transfer direction of nitrogen on the interface of the sediment-water<sup>14,15</sup>. However, limited information is available about how many forms of nitrogen exist in the sediments and how they distribute, which form can take part in the cycling easily and how much the different forms of nitrogen contribute to the circulation. Therefore, it is essential to explore the spatial distributions of nitrogen form in the sediments and the relationship between the different forms of nitrogen and environmental significance.

TABLE-1  
STATISTICS OF NITROGEN FORMS IN SURFACE SEDIMENTS OF EAST LAKE AND WEST LAKE (mg kg<sup>-1</sup>)

Items	Total nitrogen	NTF-N	TF-N	IEF-N	WAEF-N	SAEF-N	SOEF-N
East Lake	Max	6454.44	5362.31	1092.14	220.05	117.13	156.87
	Min	5216.05	4187.32	834.65	97.25	56.81	53.92
	Average	5606.77	4617.95	988.82	161.32	82.05	92.82
	Coefficient of variant	0.07	0.08	0.08	0.24	0.29	0.33
West Lake	Max	5500.86	4676.05	1048.38	175.49	143.57	186.01
	Min	4942.88	4135.59	798.65	96.22	46.22	71.32
	Average	5318.92	4403.85	915.07	130.72	76.93	115.95
	Coefficient of variant	0.04	0.04	0.11	0.22	0.42	0.39

## EXPERIMENTAL

**Study area:** Both East Lake and West Lake are typical shallow freshwater lakes. East Lake, located in northeast Quanzhou city and surrounded by streets and residential areas, has a catchment area of about 7.1 hectares and an average depth of water about 1.5 meters. West Lake, in the northwest of the city, has a catchment area of about 82.28 hectares and an average depth of water about 2.5 meters. Similarly, it is surrounded by streets, residential areas and industrial areas. In addition, West Lake is an important component of city flood protection and water logging drainage project and was ever awarded the honorary title Model Prize of China Habitat Environment in 2001<sup>11</sup>.

**Sampling:** According to the sampling principles regulated in the investigation of lake eutrophication, the sampling sites in East Lake and West Lake were established in April 2008 (Figs.1 and 2). The samples were collected by grab samplers and taken to the laboratory in air-sealed plastic bags at 4 °C. They were then air-dried at room temperature and ground to pass through a 200-mesh sieve for extractable experiment. pH, temperature and other environmental factors of the overlying water were measured *in situ* and the overlying water collected was taken back for the analysis of physical and chemical properties.

**Research methods:** Through an improved sequential extraction method<sup>16,17</sup> four forms of transferable nitrogen (TF-N, they can take part in interface cycling) are extracted, including nitrogen in ion exchange form (IEF-N), nitrogen in weak acid extractable form (WAEF-N), nitrogen in strong alkaline extractable form (SAEF-N) and nitrogen in strong oxidant extractable form (SOEF-N). The first three forms of transferable nitrogen are inorganic nitrogen and SOEF-N is mainly the organic nitrogen. At the same time the total nitrogen is determined<sup>16,17</sup> and the difference between total nitrogen (TN) and the transferable nitrogen (TF-N) is the non-transferable nitrogen (NTF-N).

The mensuration of some environmental parameters, including temperature, dissolved oxygen (DO) and pH were determined by water analyzer (HORIBA W-23, Japan) *in situ*. The chlorophyll-a (Chl-a) of the overlying water was determined by multiwavelength phytoplankton pulse-amplitude-modulated fluorometry (Phyto-PAM, Germany); total organic carbon (TOC) in the sediment was analyzed through total organic carbon analyzer (Multi N/C2100, Germany).

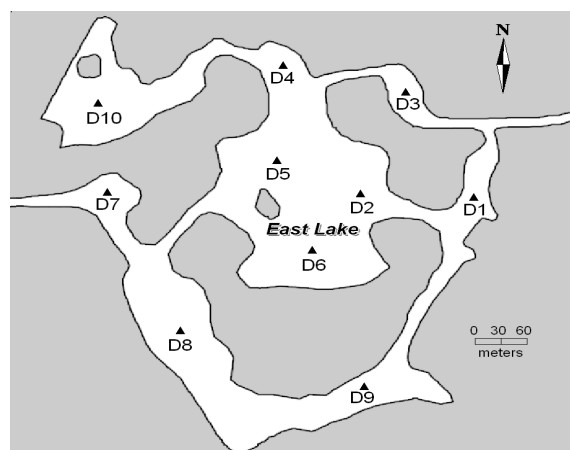


Fig. 1. Sampling sites of East Lake

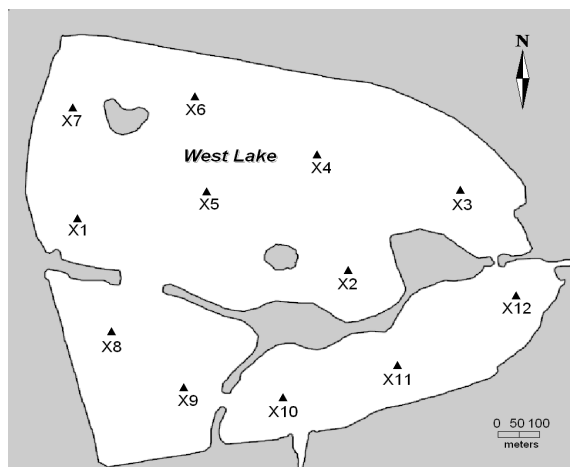


Fig. 2. Sampling sites of West Lake

## RESULTS AND DISCUSSION

**Spatial distributions of different forms of nitrogen in surface sediments:** The contents of different nitrogen forms in surface sediments of the two lakes are shown in Table-1.

**Spatial distributions of total nitrogen, NTF-N in surface sediments:** Total nitrogen in surface sediments of East Lake range from 5216.05 to 6454.44 mg kg<sup>-1</sup>, with an average of 5606.77 mg kg<sup>-1</sup>. The highest content appears at station D8 which is near to zoo. This phenomenon may be related to animal excreta containing nitrogen. The excreta are directly discharged into the lake, which causes the accumulation of nitrogen in the sediments. The lowest content lies in the station D1 near the inlet, where the flow of water might be too urgent to accumulate exogenous import (Table-1 and Fig. 3).

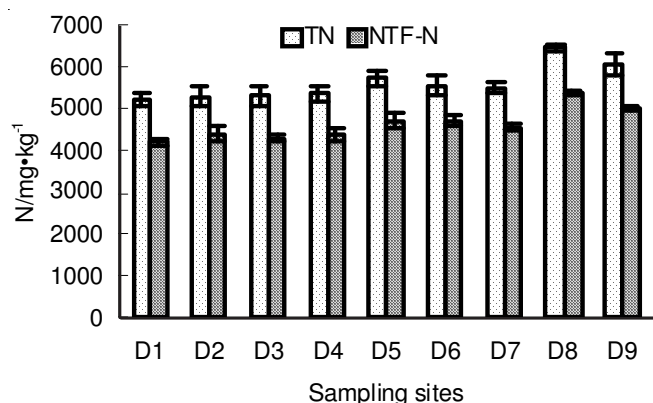


Fig. 3. Distributions of total nitrogen (TN) and NTF-N in surface sediments of East Lake

Total nitrogen in surface sediments of West Lake vary from 4942.88 to 5500.86 mg kg<sup>-1</sup>, with an average of 5318.92 mg kg<sup>-1</sup>. The highest content appears at station X5, which is in the middle of the lake. As water there flows gently, less endogenous nitrogen runs away. The lowest content is at station X1 located in northwest West Lake, because this area is far away from the inlet and less exogenous nitrogen can be accepted (Fig. 4).

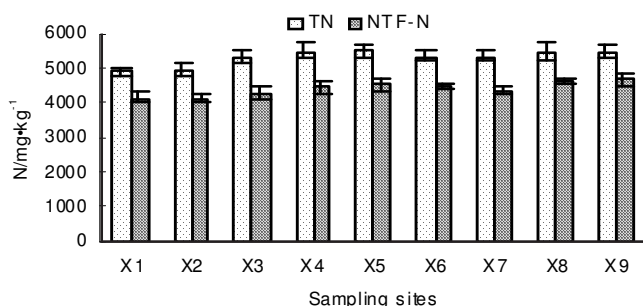


Fig. 4. Distributions of total nitrogen (TN) and NTF-N in surface sediments of West Lake

Non-transferable nitrogen in surface sediments of East Lake range from 4187.32 to 5362.80 mg kg<sup>-1</sup>, with an average of 4617.95 mg kg<sup>-1</sup>, accounting for 82.36 % of total nitrogen on average. The highest content appears at Station D8 near to zoo and the lowest at station D1 near the inlet (Fig. 3). Non-transferable nitrogen in surface sediments of West Lake range from 4135.59 to 4676.05 mg kg<sup>-1</sup>, with an average of 4403.85 mg kg<sup>-1</sup>, accounting for 82.80 % of total nitrogen on average. The highest content appears at station X2 in the middle of the lake and the lowest at station X9 in south West Lake (Fig. 4). Non-transferable nitrogen in the sediments of both lakes is the dominant form in total nitrogen.

In China, the average contents of total nitrogen in surface sediments of similar lakes are as follows: Tai Lake<sup>18</sup>, 640 mg kg<sup>-1</sup>; Dianchi Lake<sup>19</sup>, 4910 mg kg<sup>-1</sup> and Erhai Lake<sup>20</sup>, 270 mg kg<sup>-1</sup>. Total nitrogen in surface sediments of East Lake and West Lake vary from 4942.88 to 6454.44 mg kg<sup>-1</sup>, with an average of 5462.85 mg kg<sup>-1</sup>, which exceeds the average of the other lakes in China.

The sediment of eutrophic lake is characterized by enrichment of nitrogen<sup>21</sup>. The water quality of East Lake and West Lake is relatively poor<sup>12</sup>, which may be closely related to

the remigration and transformation of pollutants in the sediment. Therefore, in terms of the contents and forms, the circulation of nitrogen in the sediment may make an important contribution to the process of eutrophication in the lake.

**Spatial distributions of transferable nitrogen in surface sediments:** The four forms of extractable nitrogen (IEF-N, WAEF-N, SAEF-N and SOEF-N) are also named after transferable nitrogen because they can be released to the water body to take part in circulation under a certain condition<sup>17</sup>. Table-1 shows that transferable nitrogen in surface sediments of East Lake ranges from 834.65 to 1092.14 mg kg<sup>-1</sup> (the average 988.82 mg kg<sup>-1</sup>), which occupies from 14.89 to 19.48 or 17.64 % averagely of total nitrogen. Transferable nitrogen in surface sediments of West Lake ranges from 798.65 to 1048.38 mg kg<sup>-1</sup> (the average is 915.07 mg kg<sup>-1</sup>), which occupies from 15.02 to 19.71 % or 17.20 % averagely of total nitrogen.

The average relative contents of the different forms of the transferable nitrogen in the sediments of both lakes are presented in Figs. 5 and 6. SOEF-N is the highest (accounts for 66.00 and 64.64 % of TF-N, respectively) and WAEF-N is the lowest (accounts for 8.30 and 8.41 % of TF-N, respectively). Besides, IEF-N is higher than SAEF-N and IEF-N is the highest of inorganic transferable forms of nitrogen (accounts for 16.31 and 14.28 % of TF-N, respectively). The coefficients of variant of IEF-N, WAEF-N and SAEF-N are relatively larger. In a sense, this indicates that the three forms of nitrogen are affected more easily than SOEF-N by the environmental factors.

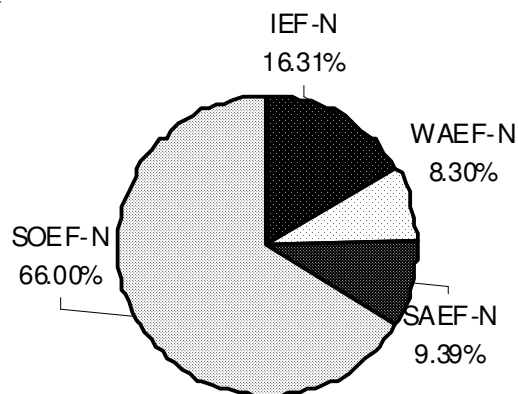


Fig. 5. Average relative content of different forms of nitrogen in the sediment of East Lake

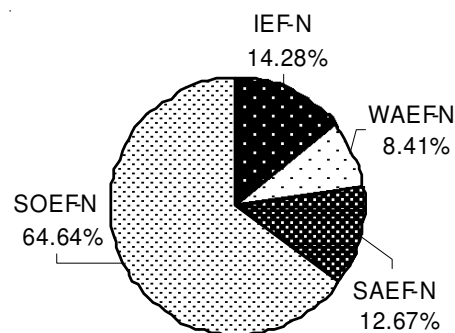


Fig. 6. Average relative content of different forms of nitrogen in the sediment of West Lake

At the station D8 of East Lake, IEF-N is the highest of all (220.05 mg kg<sup>-1</sup>). IEF-N is the adsorptive nitrogen and the

TABLE-2  
PEARSON CORRELATION COEFFICIENTS BETWEEN THE DIFFERENT FORMS OF NITROGEN  
AND ENVIRONMENT FACTOR OF EAST LAKE AND WEST LAKE (n = 9)\* > 0.05; \*\* > 0.01

Items		IEF-N	WAEF-N	SAEF-N	SOEF-N
East Lake	Temperature of overlying water	-0.53*	-0.36	-0.38	0.32
	pH of overlying water	0.38	-0.15	-0.16	0.14
	Dissolved oxygen of overlying water	0.03	0.23	0.33	-0.14
	TOC of sediment	0.51*	0.3	-0.26	0.62*
West Lake	Temperature of overlying water	-0.36	-0.21	-0.11	-0.13
	pH of overlying water	0.24	0.09	-0.38	-0.47
	Dissolved oxygen of overlying water	0.21	0.27	-0.01	-0.31
	TOC of sediment	0.73**	0.42	-0.13	0.54*

content of organic material in the sediments near to zoo is the highest, so the adsorptive capacity would be the strongest. The lowest is at station D5 in the center of lake ( $97.25 \text{ mg kg}^{-1}$ ), because external disturbances like wind waves and cruisers can accelerate the release of IEF-N in this area. The highest content of WAEF-N lies in station D2 near the inlet ( $117.13 \text{ mg kg}^{-1}$ ) due to more extraneous inputs and lower acidity of environment. The lowest content is at station D7 near the outlet ( $56.81 \text{ mg kg}^{-1}$ ), for the outlet is narrow and the rapid flow prevents WAEF-N from accumulating.

SAEF-N is dramatically fluctuated and the trend is similar to WAEF-N and the highest content, which is  $156.82 \text{ mg kg}^{-1}$  and 2.9 times the lowest, exists at station D3 nearby the inlet. SOEF-N is the dominant form that can be released to take part in recycling. The highest content of SOEF-N appears at station D9 near the zoo ( $742.72 \text{ mg kg}^{-1}$ ), because SOEF-N is mainly the organic form of nitrogen, whereas the organic matter is rich in animal excreta. The lowest exists at Station D2 near the inlet ( $540.08 \text{ mg kg}^{-1}$ ; Fig. 7).

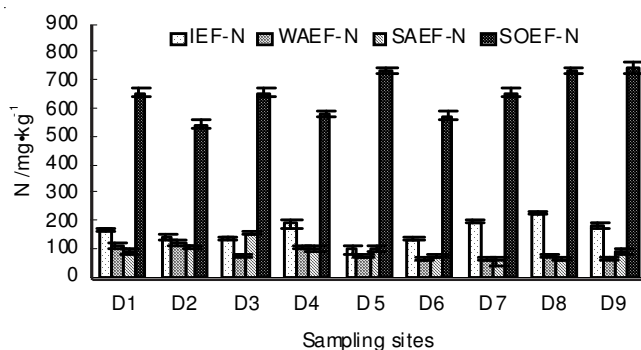


Fig. 7. Distributions of different nitrogen forms in surface sediments of East Lake

The highest content of IEF-N appears at station X7 in northwest West Lake ( $175.49 \text{ mg kg}^{-1}$ ) and the lowest exists at station X2 of central lake. The content of WAEF-N has a large fluctuation and the highest content, which is  $143.57 \text{ mg kg}^{-1}$  and 3.1 times the lowest, also appears at station X7. The highest content of SAEF-N appears at station X4 in the middle part of West Lake and it is  $186.01 \text{ mg kg}^{-1}$ , 2.6 times the lowest. This reflects that different stations have various oxidation environments. The highest content of SOEF-N appears at station X3 near the inlet ( $717.70 \text{ mg kg}^{-1}$ ), because sampling spot accepts more extraneous import. The lowest exists at station X1 in northwest West Lake ( $490.89 \text{ mg kg}^{-1}$ ), as the spot lies in semi-closed lake-bay and then it can accept little extraneous input (Fig. 8).

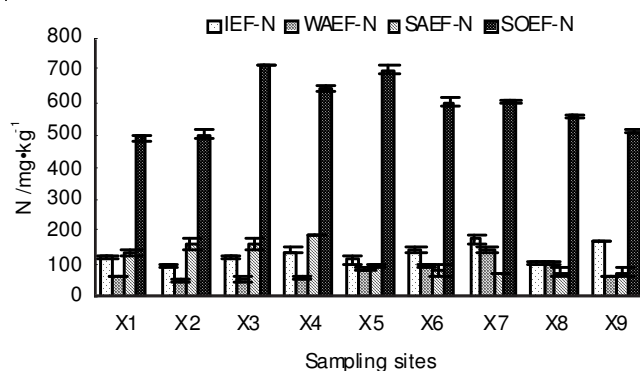


Fig. 8. Distributions of different nitrogen forms in surface sediments of West Lake

**Relationship between different forms of nitrogen and environmental factors:** Existing forms and distributions of nitrogen in the sediments are affected by many environmental factors, such as temperature, pH, dissolved oxygen of overlying water and TOC in sediment, *etc.* These factors affect the formation and release of nitrogen in sediments, which largely controls the existing forms, the contents and the distributions of nitrogen in the sediments<sup>4</sup>. Table-2 shows the Pearson correlation coefficients between various forms of nitrogen and environmental parameters of both lakes.

The correlations between different forms of nitrogen and affecting factors are discussed in Table-2.

**Effect of temperature:** The four forms of transferable nitrogen in sediments of both lakes are negatively correlated with temperature of the overlying water to various degrees (except for SOEF-N in East Lake), which illustrates that the temperature has the similar impact on the formations and releases of the four forms of nitrogen in the sediments (Table-2). Theoretically, temperature can directly affect the process of mineralization of organic matter in the sediments (such as SOEF-N), which leads to the lower content of the organic forms of nitrogen<sup>16</sup>.

As for the inorganic forms of nitrogen, the rise of temperature has a direct impact on adsorption of the different forms of nitrogen in sediments (such as IEF-N, WAEF-N, SAEF-N), which simultaneously speeds up the activities of the benthos and strengthens the role of biological disturbance. Accordingly, as the release of the different forms of inorganic nitrogen in sediments is enhanced, the contents of different forms of inorganic nitrogen decrease<sup>22</sup>. In short, a higher temperature can speed up the release of different forms of nitrogen in sediments.

TABLE-3  
PEARSON CORRELATION COEFFICIENTS AMONG THE CONTENTS OF DIFFERENT FORMS OF NITROGEN AND THE TOTAL NITROGEN, CHLOROPHYLL-A OF OVERLYING WATER OF EAST LAKE AND WEST LAKE (n = 9) \* > 0.05; \*\* > 0.01

	Items	IEF-N	WAEF-N	SAEF-N	SOEF-N
East Lake	Total nitrogen of overlying water	0.53*	0.14	0.29	0.73**
	Chlorophyll-a of overlying water	0.26	-0.09	-0.23	0.52*
West Lake	Total nitrogen of overlying water	0.47	0.1	0.44	0.68*
	Chlorophyll-a of overlying water	0.31	0.02	-0.19	0.24

**Effect of pH:** IEF-N and SOEF-N of East Lake are positively correlated with pH of the overlying water, while IEF-N and WAEF-N of West Lake have positive correlation with pH. The reason is that higher pH gives the sediment a relatively oxidative condition and correspondingly nitrification is relatively stronger<sup>23</sup>. The dominant form of nitrogen in IEF-N and SOEF-N of East Lake is nitrate nitrogen ( $\text{NO}_3^-$ -N) and dominant form of nitrogen in IEF-N and WAEF-N of West Lake is nitrate nitrogen ( $\text{NO}_3^-$ -N), too. So pH has more correlation with these forms of nitrogen.

**Effect of dissolved oxygen:** IEF-N, WAEF-N and SAEF-N are approximately positively correlated with dissolved oxygen of the overlying water (except SAEF-N in East Lake) and the SOEF-N has negative correlation with dissolved oxygen. Because higher dissolved oxygen creates a relatively oxidative condition in sediments. Therefore, more organisms are decomposed to take part in cycling through the sediment-water interface and inorganic nitrogen increase. Although the benthos gets more active, which promotes the release of inorganic nitrogen, mineralization of organic matter in the dissolved oxygen-rich lake area is in a dominant process<sup>24</sup>.

**Effect of total organic carbon:** Total organic carbon (TOC) is an indicator for organic matter in sediments<sup>25</sup>. As can be seen from Table-2, IEF-N, WAEF-N and SOEF-N in the sediments of both lakes has a positive correlation with TOC to a certain extent and SAEF-N is negatively correlated with TOC, which may be closely linked to formation of different forms of nitrogen, nature of the sediment and the bonding strength. As IEF-N is adsorptive nitrogen, the higher the content of organisms in the sediments, the stronger the adsorptive capacity. So IEF-N is positively correlated with TOC. The formation and distribution of WAEF-N mainly depends on the content of carbonate in the sediments and pH change during the processes of organisms' mineralization<sup>26</sup>.

In general, if the content of carbonate gets higher in the sediments with lower TOC, TOC mineralization would be weaker and consequently, pH variation would be smaller. The dissolution and deposition of carbonate would also be weaker, so WAEF-N would be lower<sup>27</sup>. Both lakes are close to industrial area, where population is concentrated and large organisms are discharged into the lakes. Higher TOC in sediments results in the stronger mineralization of TOC which would causes wide variation of pH and higher WAEF-N, so WAEF-N has a positive correlation with that of TOC. SOEF-N, as the dominant component of organisms, has a similar digenetic process and transfer mechanism with TOC. Therefore, SOEF-N is positively correlated with TOC. Besides, the distribution of SAEF-N is mainly controlled by the oxidative-reductive condition. The higher the content of TOC in the sediments is, the stronger the reduction of sediment would be and SAEF-N would be lower<sup>28</sup>, so SAEF-N is negatively related to TOC.

**Environmental significance of transferable nitrogen in sediments:** Biogenic nitrogen, one of necessary nutrients for phytoplankton has an important effect on change of biological populations. Nitrogen even can become the limiting factor in the growth of phytoplankton, so nitrogen in sediments has close relation to the distribution and abundance of phytoplankton<sup>29,30</sup>. Chlorophyll-a (phytoplankton standing stock) has no direct relation with sediment, but it can indirectly interact and affect sedimentary early diagenesis through other physical, chemical or biological processes, thus, to some extent affects the forms and contents of nitrogen in sediments<sup>31</sup>. Table-3 shows the Pearson correlation coefficients among the contents of various forms of nitrogen and total nitrogen, chlorophyll-a of the overlying water.

The different forms of nitrogen in sediments of both lakes basically show a positive correlation with total nitrogen of the overlying water, while IEF-N and SOEF-N have significantly positive correlation with total nitrogen. This shows that these two forms of nitrogen make more contributions to biogeochemical cycles and that the overlying water has the controlling function on the transferable nitrogen (Table-3). Chlorophyll-a, an important index of measuring primary productivity, interacts with the sediments through a series of physical, chemical reactions and biological activity<sup>32</sup>. The study shows that IEF-N, SOEF-N in the sediments of both lakes have a positive correlation with chlorophyll-a of the overlying water and that SAEF-N has a negative correlation with chlorophyll-a, whereas WAEF-N and chlorophyll-a have a poor correlation. These suggest that the releases of IEF-N and SOEF-N of both lakes make more contributions to the growth of phytoplankton.

As the bonding strength of IEF-N is the weakest, when a slight change or disturbances appear, it is likely to be released into the overlying water and take part in the cycle. The production status of phytoplankton affects the changes of nutrients in water. When nutritional materials in water decrease significantly due to increasing consumption, IEF-N in the sediments may be released into overlying water to supply for primary productivity. Therefore, IEF-N and chlorophyll-a have a good correlation. In addition, if the content of chlorophyll-a in water area gets higher, the photosynthesis would be stronger, the growth of phytoplankton would be more active and the excreta containing abundant organic matter would be decomposed and mineralized during the constant sedimentation and suspension. Also a large amount of dissolved oxygen is consumed with the prosperous growth of phytoplankton. As a result, the decomposition and mineralization of organic matter are relatively weakened and the content of SOEF-N gets higher when the decomposition rate of organisms gets lower than the sedimentary rate<sup>31</sup>. Therefore, SOEF-N and chlorophyll-a have a positive correlation.

## Conclusion

(1) The average contents of total nitrogen in the surface sediments of East Lake and West Lake are 5606.77 mg kg<sup>-1</sup> and 5318.92 mg kg<sup>-1</sup>, respectively, which exceed the average of major lakes in China; NTF-N is the dominant form in total nitrogen; TF-N accounts for 17.64 and 17.20 % of total nitrogen, respectively. The average contents of different forms of nitrogen in the surface sediments of two lakes are in the order, SOEF-N > IEF-N > SAEF-N > WAEF-N and SOEF-N is the dominant form in TF-N (accounts for 66.00 and 64.64 % of TF-N, respectively). In addition, IEF-N is the highest of the inorganic transferable forms of nitrogen (accounts for 16.31 and 14.28 % of TF-N, respectively). The spatial distributions of various forms of nitrogen are different;

(2) Pearson product-moment correlation coefficient shows that IEF-N has a positive correlation with TOC in the sediments, pH and dissolved oxygen of the overlying water; WAEF-N is positively correlated with dissolved oxygen of the overlying water and TOC in the sediments; SAEF-N and dissolved oxygen of the overlying water show a positive correlation; And SOEF-N is positively correlated with TOC. In a word, four forms of transferable nitrogen are not affected obviously by temperature, pH and dissolved oxygen of the overlying water, although they are interacted reciprocally.

(3) IEF-N and SOEF-N are positively correlated with total nitrogen and chlorophyll-a of the overlying water; and WAEF-N and SAEF-N are positively related to total nitrogen of the overlying water, which indicates that the sediments have a non-negligible effect on the content of the elements of the overlying water. Meanwhile the results show that nitrogen in sediments is a good indicator of lake eutrophication, therefore, it has a very important environmental significance.

## ACKNOWLEDGEMENTS

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