

## Insight into the spatial distribution of nutrient elements and sediments fraction analysis in Taihu Lake

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### ABSTRACT

Lake eutrophication in China is a serious issue and has raised urgent attention, which is required for a better understanding of the eutrophic status. Particularly, the eutrophication of shallow lakes has received public attention for shallow lakes are vulnerable to changes in eutrophic status due to the closer proximity with bottom lake sediments. Herein, a comprehensive investigation on the spatial distribution of nutrient elements (including carbon, nitrogen and phosphorus) was conducted in a typical large shallow lake Taihu Lake, and the internal patterns between the distribution and eutrophic status were analyzed. The results showed that the distributions of nutrient elements in surface sediment displayed spatial diversity in different regions. Zhushan Bay, East Taihu Lake and Dongjiaozui Bay hold distinguished pattern of nutrient contents due to the different geographical locations and economic pattern of adjacent areas. Specifically, the concentrations of total carbon and total nitrogen in East Taihu Lake were significantly higher than other areas, and total phosphorus content in Zhushan Bay was the highest. Furthermore, different phosphorus fractions in sediment and eutrophic indicators of water column were further analyzed to reveal the potential contribution of sediments to nutrient loadings of overlying water. The phosphorus fraction analysis suggested that calcium bounded phosphorus accounted for the main component. Correlation analysis revealed the internal relations among various characteristics in sediment or water, which indicated that microcystis blooms were accompany with excessive COD and phosphorus and depletion of dissolved oxygen. The results offered a comprehensive understanding of the lake eutrophic status and benefited further the study on the ecological status assessment.

*Keywords:* Nutrient elements; Spatial distribution; Phosphorus fraction; Surface sediment; Correlation analysis

### 1. Introduction

As a result of serious water pollution and intensive human activities, most of fresh lakes are becoming eutrophic. The eutrophication of surface waters has raised more and more public attention for it is becoming a serious environmental problem [1]. The eutrophication process can result in abnormal phytoplankton increase,

water transparency decrease, water quality deterioration and finally the water function forfeiture. Due to the excessive discharge of pollutants containing nitrogen and phosphorus from point and non-point sources, the pollutant concentrations exceeded the basin's environmental carrying capacity and caused serious threaten to ecological safety. Taihu Lake, located in eastern China, is the third largest freshwater lake in China. Along with the rapid industry development and population increase, intensive water resources were consumed and the water quality was getting more and more seriously polluted.

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The eutrophication status of Taihu Lake became worse in recent years although different areas of the lake have different eutrophic status. Recently, the contents of nutrient elements (including N and P) increased annually, and the concentrations of TP in several areas were more than 0.25 mg/L [2]. Especially for the north regions, algal blooms have occurred with increasing frequency in the areas of Zhushan Bay and Meiliang Bay, which caused severe crisis due to the shortage of drinking water [3]. As shown in Fig. S1 (Supplementary Material), the eutrophic status was serious and amazing and the government spent over 14 billion dollars to clean up Taihu Lake [4]. As one of the typical shallow lakes, Taihu Lake has a water depth of less than 5 m, are generally unstratified. Due to the “shallowness”, the overlying water and underlying sediment interact frequently and non-periodically [5]. The lakes on lowland plains are generally shallow and sensitive to human activities, which are vulnerable to water pollution [4,6]. In China, most fresh lakes were considered as shallow lakes. Therefore, the investigation on the eutrophic status of Taihu Lake, the 3<sup>rd</sup> largest freshwater lake in China, is of great significance to the water resource protection and ecological health.

Generally, the bottom sediments were considered to play a vital role in lake ecosystem dynamics, both as a sink and source of nutrients, thereby strongly influenced lake trophic status and biodiversity [7]. In detail, the lake sediments involved in nutrient cycle, such as physical, chemical and biological processes of C, N and P. Significantly, surface sediment is the most active part in the interaction between water column and sediment, and the release of nutrient elements from sediment might also result in the eutrophication [8,9]. Owing to the unique properties of shallow properties, the importance of lake sediments as a nutrient sink and a nutrient source has long been recognized [10]. Knowledge of sediment nutrient abundance and availability in lake bottom sediments is therefore of critical importance for understanding and predicting whether a lake ecosystem is in equilibrium with its external nutrient loading.

Phosphorus is an essential biogenic element for all life forms and closely associated with societal concerns. In biogeochemical cycles, phosphorus is a critical element for aquatic ecosystem and excessive P will accelerate freshwater productivity, therefore P is regarded as the key factor in freshwater eutrophication [11]. Generally, external inputs and sediment release were two main sources of P loadings to the overlying water. With the industrialization development and population growth, phosphorus flux from land to water increased clearly. Phosphorus in runoff from agricultural land is an component of source pollution and can accelerate eutrophication of lakes and streams [6,12]. In the study conducted by Jaivie et al., drainage was proved to provide a greater P sink than previously considered, and the retained P became a long-term source of slowly released P to surface waters [13]. High loading of phosphorus led to high phytoplankton biomass, turbid water and often undesired biological changes, and that phosphorus arrives in natural aquatic ecosystems and accumulates in sediments which act as a sink for phosphorus [4,8]. Sedimentary phosphorus was observed by Gao to be released to the water column when the sur-

rounding conditions changed, and the mechanisms were different in various conditions for the phosphorus release potential strongly relied on sediment properties such as pH and redox potential [14]. Therefore, a dynamic balance of phosphorus between the sediment and water column would be beneficial to our understanding on lake eutrophication mechanisms and controlling methods. In most lakes, P is transported to the lake by catchment drainage, and is generally associated with solids of iron (Fe), aluminum (Al), and calcium (Ca) [15]. Fractionation schemes as a method to characterize phosphorus binding to a variety of organic and inorganic sediment components have been widely used in literatures [16,17].

It is of significance to evaluate the distribution characteristic of nutrient element and forms of phosphorus in the sediments. Accurate information on the distribution pattern and component contents is beneficial for future management of the lake [18]. In this study, a large number of surface sampling stations were studied, and the specific concentrations of various element and constituent in sediment were determined. For water column, different parameters of water quality were determined to assess the eutrophic status. In addition, a thorough data analysis on the correlation was conducted. The aim of this research is to define the P fractions, the concentrations and the spatial distributions of carbon, nitrogen and phosphorus forms of Taihu Lake, and then to evaluate the immediate and potential contributions to the water column. This research is favorable to a better understanding of the evolution of the sediment environment of Taihu Lake, and affords plentiful information for further studies on the mechanism and restoration of lake eutrophication.

## 2. Materials and methods

### 2.1. Study sites

Taihu Lake is located in the Yangtze River delta in eastern China which between 30°92'34"–31°54'00" N and 119°90'00"–120°61'82" E, which is a large, shallow (mean depth = 1.9 m), eutrophic lake, with a large surface area of 2338 km<sup>2</sup> and a volume of 4.4 billion m<sup>3</sup> [1]. It plays an important part in people's daily life and industrial production in the region as a multifunctional supplier for drinking water, irrigation, aquaculture and industry.

### 2.2. Sediment sampling

The Taihu Lake was divided into 190 sites according to the locations. Among the 190 sites, 28 sites were missed because of the lie waste and other reasons. In total, 162 sites were selected for sampling in this study (Fig. 1). Also, Taihu Lake consists of 12 lake areas, and each area contains several sampling sites. The approximate locations of all lake area and the corresponding numbers of sampling sites in every lake area are displayed as different colours.

The specific sampling procedure was as follow. Surface sediment samples were collected using a Peterson grab sampler. These samples were stored in sealed plastic bags and transported to the laboratory for further treatment. The collected samples were dried naturally at room tem-

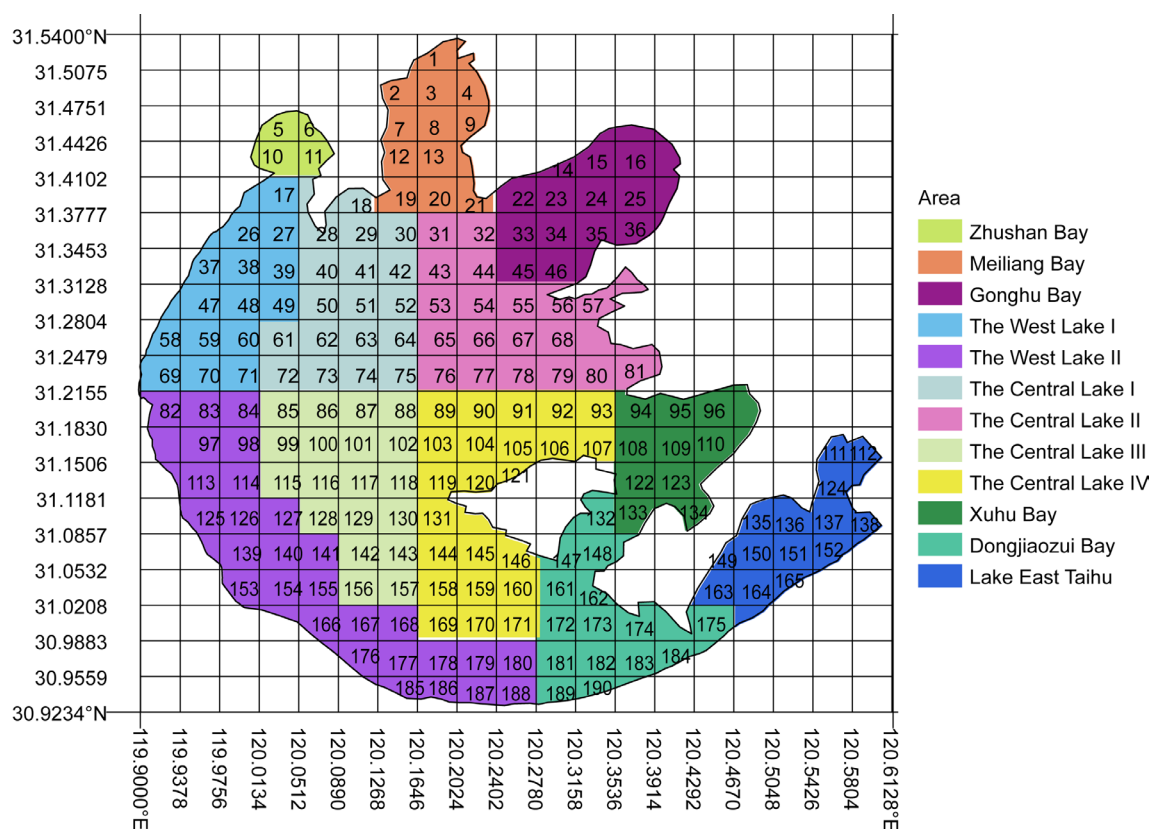


Fig. 1. Map of the study area and sampling sites.

perature, grounded in the IKA A11 basic analysis mill and screened with a 100 mesh sieve, and stored in plastic bottles for analysis.

### 2.3. Analytical method

The  $\text{HClO}_4\text{-H}_2\text{SO}_4$  digesting methods were used to analyze the total phosphorus (TP), and the measurements of total nitrogen (TN) and total carbon (TC) were performed using Thermo Flash 2000 elemental analyzer (Cambridge, UK). Loss on ignition (LOI) was measured by combusting the sample for 4 h at 550°C. Carbonate content (CC) was calculated according to the mass difference between 550 and 900°C (for 1 h) using the formula: mass difference (550–900°C) \* 227/dry weight. Mineral matter contents (MMC) were calculated using the equation  $100\text{-LOI-CC}=\text{MMC}$  as percent of dry weight [19]. Phosphorus fractionation analysis was carried out according to an improved method [20], in which the phosphorus in sediment was divided into (exchangeable phosphorus) Ex-P, aluminum-bound phosphate (Al-P), iron-bound phosphate (Fe-P), occluded phosphate (Oc-P) and calcium-bound phosphate (Ca-P). The methods for the estimation scheme were proposed by Zhou [17]. The measurements of pH and dissolved oxygen were conducted by F-20 pH/mV Meter (Beijing Qiyuan Electronic Instrumentation Co., China) and DO-11P (TOA Electronics Ltd., USA) respectively, and chemical oxygen demand (COD) and biological oxygen demand (BOD) of the water were determined according to the standard meth-

ods [21]. For the sediment, the grain size were obtained by a Mastersizer 2000 Laser Size Analyzer (Malvern Co., UK) and the data were classified into three categories: sand (0.05–2 mm), slit (0.002–0.05 mm) and clay (<0.002 mm).

### 2.4. Statistics methods

The principal component analysis (PCA) was used to seek out nutrient distribution pattern using package “vegan” in R. The correlation analysis was conducted by corrplot package in R software to reveal the inner relationship between the eutrophic state and characteristics in sediment or water.

## 3. Results and discussion

### 3.1. Surface sediment characteristics and overall elemental content

Prior to specific nutrient element distribution, the analysis of surface sediment and overlying water characteristics was conducted. The properties of sediments and overlying water determined the status of lake [9], so the relevant physical and chemical parameters were investigated in the current study. The characteristics of overlying water and sediments were shown in Table S1 and S2 (Supplementary Material). According to the results, the pH of overlying water across the lake was about neutral, and alkaline pH

value was observed for sediment. About the size distribution, slit was the predominant fraction. The results of LOI (1.35%–11.71% of dry mass) showed that low organic matter content was detected in the sediment. Then, the CC was only 1.05%–6.38% of dry mass, but the MMC accounted for 82.61 to 96.85% dry mass. Therefore, MMC occupied the major part of sediment. In specific regions of Taihu Lake, high values of LOI were obviously spread across the Meiliang Lake and East Taihu Lake. On the contrary, lowest contents of mineral matter were observed in these regions (Fig. S2 (Supplementary Material)). High organic content across the East Taihu Lake was probably due to macrophyte vegetation, whereas the high organic content in Meiliang Lake results from a combination of sources, i.e. allochthonous organic matter, urban sewage and human input.

The chemical component concentration of nutrient element (TP, TC and TN) and various forms in the surface sediments were displayed in Table 1, and the data showed significant diversity for the contents varied in an extensive range. To acquire a whole profile of the nutrient concentration of Taihu Lake, the concentrations of TP, TC and TN in sediments were measured and statistic distributions patterns were shown in Fig. 2. For example, the contents of TP showed a widely distribution range from 0.16 to 2.32 mg/g in the sediments over the whole Taihu Lake, and the average concentration was about 0.5 mg/g. The highest concentration (2.32 mg/g) was 4.6 times of average TP level, which suggested the unbalanced TP distribution across the whole lake area. The studies on the phosphorus content in various rivers or lakes were conducted to analyze the eutrophica-

tion status. It was found that for most lakes in China, the phosphorus content in surface sediments was less than 0.25 mg/g, and few lakes have TP above 0.75 mg/g [11]. In this study, most of the TP value was in the range of 0.25–0.75 mg/g, and the maximum was close to the content in Waihai. The results indicated that some regions in Taihu Lake were at serious eutrophication. In addition, the TC and TN exhibited similar distribution patterns as Fig. 2b and 2c depict, and the highest contents were 5.3 and 5.7 of the mean TC and TN concentrations respectively. Due to the complexity of influencing factors, the clear thresholds of nutrients for eutrophication were difficult to determined, and this threshold was specific for each lake. Given the importance of sediment-water interactions, a variety of changed conditions such as temperature fluctuation and hydraulic disturbance could resulted in the variations of eutrophic state as well as nutrient distribution in sediments [22]. Despite the unbalance distributions of nutrients across all the lake areas, the partial high concentrations of nutrient elements would be sensitive to ambient conditions or human activities, which might led to the switch to a eutrophic state in partial lake areas or even the whole Taihu Lake.

### 3.2. Spatial distribution of nutrient elements in Taihu Lake

To better analyze the spatial distribution of these nutrient elements, the TP, TC and TN concentrations in different area are shown in Fig. 3. It was clear that the central water area exhibited healthy status for the relative low nutrient content. However, the lake near to land was shown to be

Table 1  
Chemical component concentrations in studied surface sediments

Parameters	TP (mg/g)	TC (mg/g)	TN (mg/g)	Ex-P (mg/g)	Al-P (mg/g)	Fe-P (mg/g)	Oc-P (mg/g)	Ca-P (mg/g)	LOI (%)	CC (%)	MMC (%)
Min	0.16	4.13	0.16	0.00008	0.00453	0.00162	0.05881	0.04036	1.35	1.05	82.61
Max	2.32	47.33	4.83	0.01767	0.19753	0.37551	0.31641	0.33310	11.71	6.38	96.85
Mean	0.50	8.86	0.85	0.00260	0.01745	0.05150	0.13123	0.13928	4.26	3.31	92.43
SD	0.21	6.14	0.64	0.00220	0.01813	0.05316	0.04388	0.04692	1.43	0.79	1.87

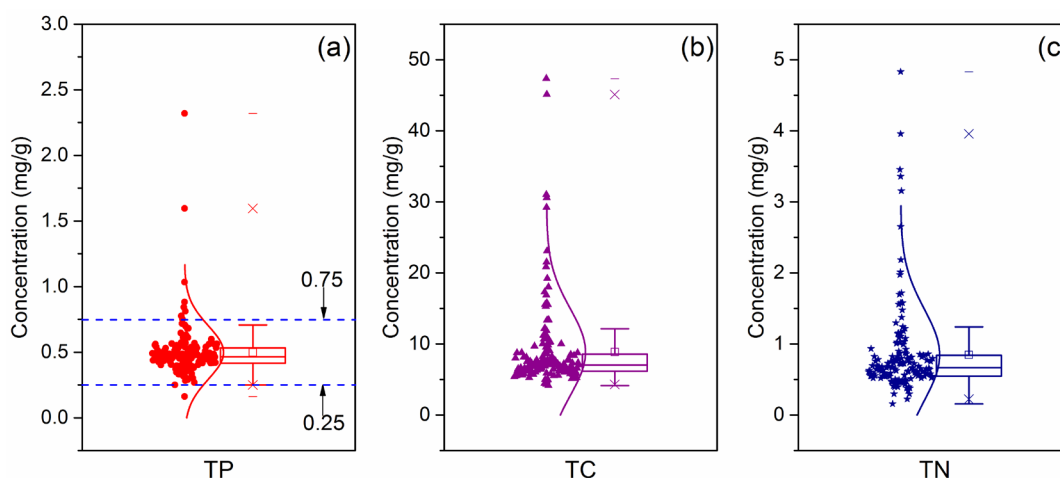


Fig. 2. The statistic distributions of TP (a), TC (b) and TN (c) in all sites surface sediment of Taihu Lake, China.



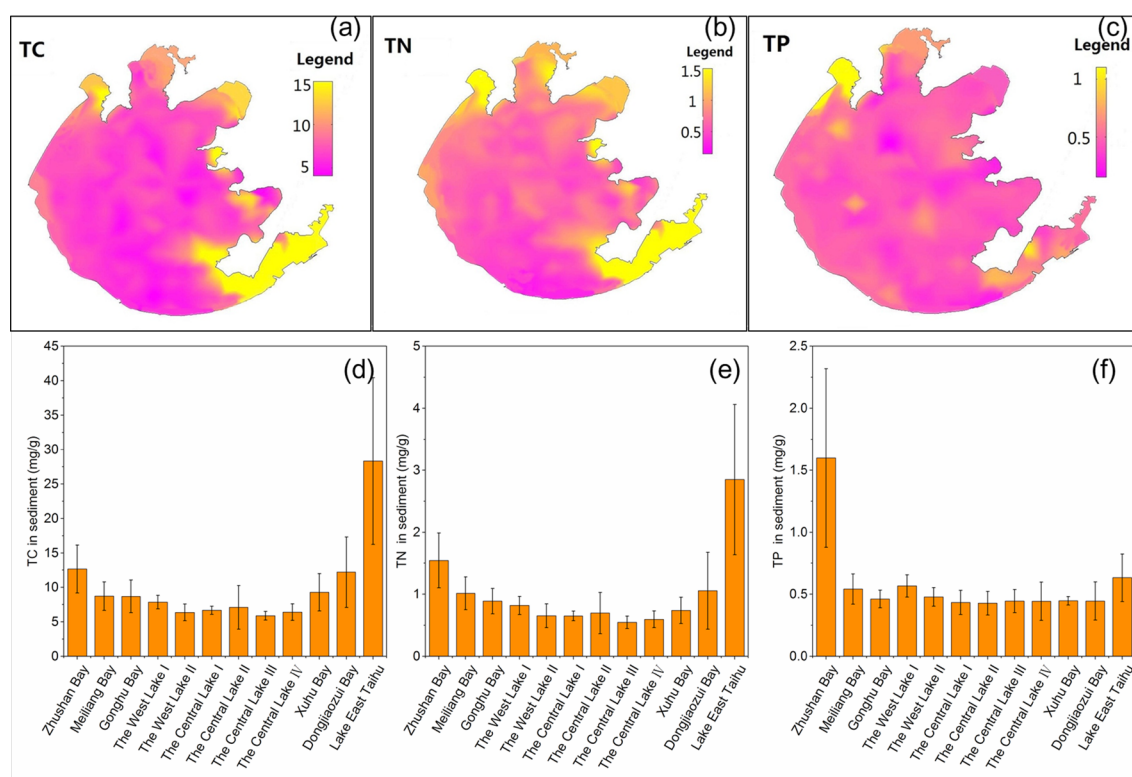


Fig. 3. The spatial distributions of TC (a), TN (b) and TP (c) in surface sediment of Taihu Lake, China; the concentrations of TC (d), TN (e) and TP (f) in different regions.

in serious eutrophic status. In detail, the Zhushan Bay (the northwest area of Taihu Lake) had the highest TP content, and the high concentrations of TN and TC were found in East Taihu Lake. Generally, ambient industrial and agriculture inputs were considered as important anthropogenic nutrient sources. Considering the geographical position, the northwest part of Taihu Lake was adjacent to urban districts and immense farm belt and linked with polluted inflowing rivers [23], and the excessive usage of fertilizer led to high phosphorus loading in Zhushan Bay. East Taihu Lake is surrounded by Wujiang District and other rural towns of Suzhou city. As is known to all, textile industry is well developed in Suzhou city, especially in these districts. In the textile industry, dyeing process uses large volume of water for dyeing, fixing and washing processes, and the generated wastewater contains high amount of dissolved solids, un-reacted dyestuffs and other chemicals [24]. Based on the constituents, dyeing and textile wastewater has high COD and TN concentrations, and the treatment is difficult and rather low efficient. Therefore, the effluent of these industries accounted for the unbalanced nutrient distribution.

For a visualized and overall understanding of the nutrient element distribution in different lakes, principal component analysis (PCA) was adopted to perform the data and the results are shown in Fig. 4. Among these lake areas, three areas, Zhushan Bay, Lake East Taihu and Dongjiaozui Bay, were obviously distinguished from others. According to the PCA results of three main factors (TC, TN and TP), Zhushan Bay possessed the highest level of TP, and the contents of TC and TN in Dongjiaozui Bay and Lake East Taihu were

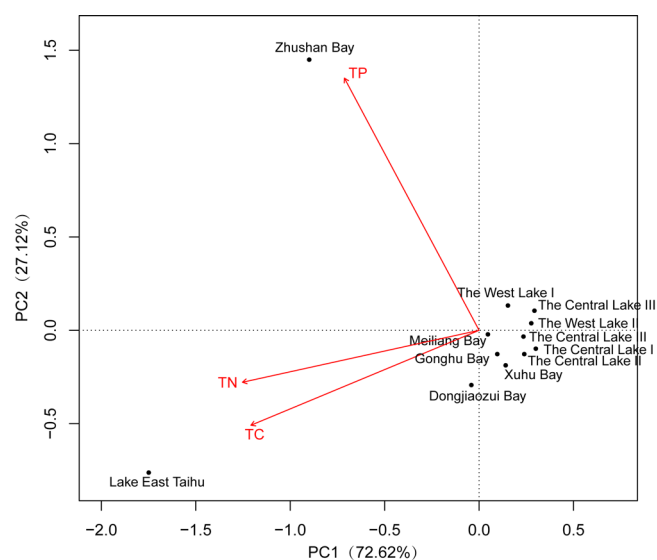


Fig. 4. The principal component analysis of TC, TN and TP of different lake areas.

much higher than others. Besides, there was a great positive correlation between TC and TN of sediments across all the lakes for correlation coefficient was 0.98, which implied that the elements of carbon and nitrogen always existed simultaneously in Lake Taihu. Except for Zhushan Bay and Lake East Taihu, other areas were in similar eutrophic patterns.

Apart from the nutrient element content, the ratios of carbon/nitrogen (C/N), nitrogen/phosphorus (N/P) and carbon/phosphorus (C/P) should also be investigated for the relation with lake eutrophic status. Previous research had proved that the C/N ratio between 8.6 and 13.6 indicated a moderate degree of N deficiency [25]. Across the whole Taihu Lake, average C/N was about 11.06, which indicated that the entirety lake was under the circumstance of nitrogen shortage. In addition, the maximum and minimum were 28.6 and 7.52 respectively. Also, the C/P and N/P ratios were calculated and the spatial distributions were shown in Fig. S3 (Supplementary Material), and the average C/P and N/P ratios were 18.2 and 1.7 respectively. Despite the overall situation, the C/N ratios in regions such as Zhushan Bay, Meiliang Bay, the West Lake I and Gonghu Bay were lower than the average level. Zhushan Bay and East Jiao Lake had the lowest and highest N/P ratios respectively, and C/P ratios in the East Taihu Lake and East Jiao Lake were higher than the ones in other regions. As for Zhushan Bay, the C/N value (8.2) was < 8.3, which was favorable to the growth of phytoplankton for nitrogen supply was not physiologically limiting. Moreover, Zhushan Bay had the lowest N/P (6.0) and C/P ratio (5.97). Generally, the phytoplankton chemical composition close to the Redfield ratio (C: N: P of 106: 16: 1) implied near maximal growth rate [26]. Herein, all the water areas investigated showed a higher nitrogen and phosphorus for the C: N: P was nearly 18: 1.7: 1. In some specific regions, such as Zhushan Bay, the nitrogen and phosphorus contents were abundant, and phosphorus was even excessive compared to other regions, so a considerable portion of the phosphorus in the surface sediments is associated with inorganic material [18].

### 3.3. The presence of various phosphorus forms in surface sediments

Phosphorus is an essential element for all life forms, and different form played differential roles in eutrophication. The potential release of P from sediments to water column depends on the form of P in sediments due to the different properties in water-sediment surface. Table 1 showed the concentrations of total and various forms phosphorus, and inorganic phosphorus (IP, the sum of Ex-P, Al-P, Fe-P, Oc-P and Ca-P) accounted for 68% of TP. Furthermore, the relative contributions of different P fraction to TP in the whole Taihu Lake were present in Fig. 5. It can be concluded that most phosphorus in the surface sediment was existed in the forms of Ca-P (40.72%) and Oc-P (38.36%), and the corresponding concentrations were 0.04036–0.3331 mg/g and 0.05881–0.31641 mg/g respectively. The content of these P fractions was in the rank order of Ca-P Oc-P Fe-P Al-P Ex-P, and this distribution pattern was similar to the situations in the Dianchi Lake in China [10].

Due to the diverse properties of various forms of phosphorus, it was necessary to analyze the specific component concentration and distribution. Ex-P represented the loosely adsorbed P in the sediments, and this fraction may include dissolved P in the pore water [27]. Thus Ex-P was considered to be immediately bio-available. Previous publication had reported that the Ex-P was released from  $\text{CaCO}_3$  associated P or decaying cells of bacterial biomass in depos-

ited phytodetrital aggregates and it was seasonally variable pool [28]. In Taihu Lake, the mean content of Ex-P in sampling sites was about 0.0026 mg/g, which contributed to 0.52% of TP.

The Al-P and Fe-P were bound up with the pollution status. Fe-P has been shown to be a potential variable component of sedimentary phosphorus, and it could also be used to determine the source of phosphorus and indicated the extent of environmental pollution. Anthropogenic phosphorus would bind to aluminum and iron oxides/hydroxides firstly in the surface sediments of Taihu Lake. Therefore, it can be explained furthermore that the Al-P and Fe-P content in Meiliang bay, Zhushan bay and Gonghu bay were higher than other regions except for the East Taihu Lake. The Al-P and Fe-P can be used for the evaluation of algal available P [29], for the release favored the growth of phytoplankton. Due to the exchangeable property with hydroxylion, the Al-P and Fe-P would be released to the water column if the pH and DO of surrounding were changed [10]. The presence of macrophyte would change the sediment condition, and Fe-P was proved to have a variable potential mobility, which depended on the conditions (such as pH and anoxic-oxic status) of sediments [30]. In this study, the East Taihu Lake was grass type lake district, so the growth of submersed macrophyte promoted the release of Fe-P.

Other than the above mentioned forms of phosphorus, Oc-P and Ca-P were considered to be bio-unavailable. Ca-P was sensitive to low pH and mainly consisted of natural and detrital apatite phosphorus in which the phosphorus was bounded to carbonates and traces of hydrolysable organic phosphorus. Phosphorus bounded to calcium was a relatively stable fraction of sedimentary P and contributed to a permanent burial of P in sediments [31]. As shown in Fig. 5f, Ca-P was the major form of IP in surface sediment of Taihu Lake. According to the spatial distribution of Ca-P, the contents in East Taihu Lake, East Jiao Lake, Xu Lake, Southwest Coast Lake and South area of the central lake were higher than the data in Meiliang Bay, Zhushan Bay and North area of the central lake. This was in accordance with the results in previous literature [32], and the high Ca-P might attributed to the calcareous terrain of the recharge area. Besides, the investigation of lakes with various trophic statuses suggested that high levels of calcium mineral-P were also observed, and Ca-P and residual-P were predominant portions accounting for 35%–90% of TP [33].

Among these phosphorus forms in sediment, bio-available phosphorus (BAP) has been defined as the sum of the phosphorus which could be transformed into available forms by natural processes [10]. Previous studies used sequential chemical extraction methods to estimate the bio-availability of sedimentary P [17], and in present study, the BAP was calculated by the sum of Ex-P, Al-P and Fe-P. The measured results showed that the BAP content in surface sediments of Taihu Lake varied from 0.0110 to 0.5907 mg/g, and Fig. S4 (Supplementary Material) depicted the spatial distribution of BAP in Taihu Lake and the concentration in different regions. It was obvious that the concentrations of BAP in Zhushan Bay and Meiliang Bay were significantly higher than other regions. The excessive BAP was attributed to the local primary production for the con-

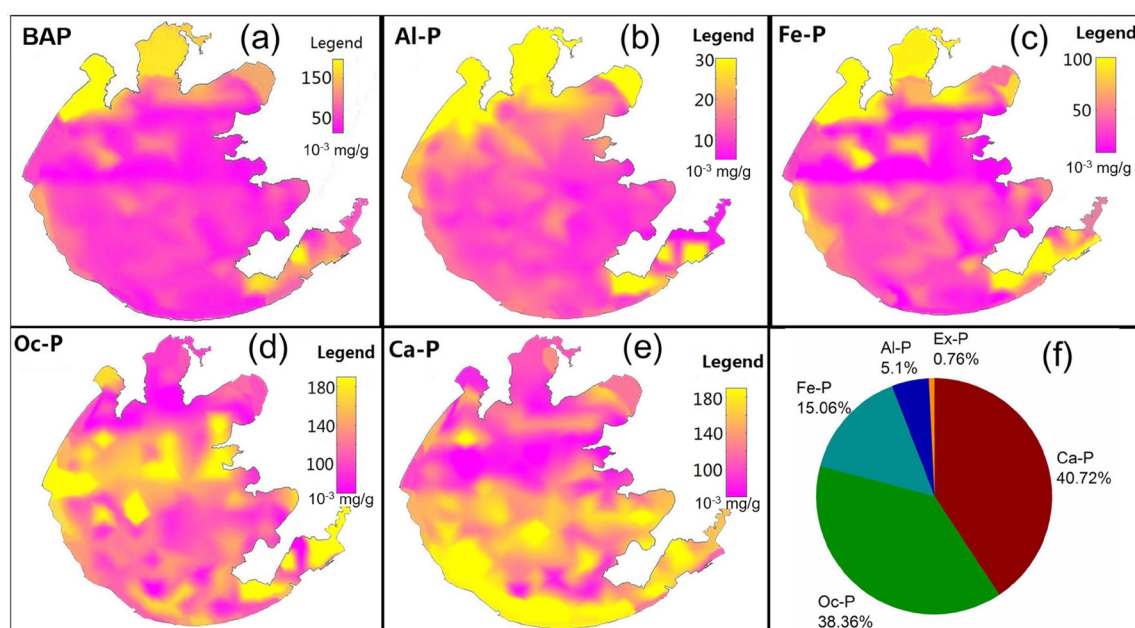


Fig. 5. Spatial distribution of phosphorus fractions (a–e) in surface sediments of Taihu Lake, and the percent of different phosphorus form (f) of the whole Taihu Lake. The unit of various forms of phosphorus is  $10^{-3}$  mg/g.

tent in water column was high in growing season, which confirmed that the BAP was seriously affected by human activities.

### 3.4. Statistical analysis of components and fractions in sediment and water column

To reveal the internal relationships between various components and fractions, the correlation analysis was conducted in this study. Firstly, the correlations between phosphorus fractions and sediment properties were analyzed and the results are shown in Table 2. The results indicated that no strong correlation was found among these parameters in sediments for all the coefficients between pairs were less than 0.60. However, moderate positive correlations (0.40–0.59) were observed between TP and LOI, which indicated that organic matters in the sediment had slight impact on the phosphorus levels of Taihu Lake. In addition, TN had moderate positive correlation with TP and Fe-P, and the corresponding coefficients were 0.42 and 0.45, while the correlations were weak between the pairs of TN vs Ex-P and TN vs Al-P.

Furthermore, the intercorrelations among various fractions in sediments and water column are analysed via the coefficient and confidence ellipse in Fig. 6. In this study, Al-P, Fe-P and BAP was positively correlated with TP (Pearson coefficient, 0.85, 0.67 and 0.67 respectively), while other forms of phosphorus (including Ex-P and Oc-P) showed moderate or weak linear correlations with TP. The data gave the evidence that the variation trends of Al-P, Fe-P, Ex-P and Oc-P were agreement with TP and the changes of the TP content were dominantly controlled by these constituents. Similar results were observed in the study on Dianchi Lake [10]. Al-P and Fe-P were bound up with the variation of TP, as well as the one of pollution status. On the contrary, it

Table 2

Pearson correlation coefficients between phosphorus fractions and the sediment properties of Taihu Lake, China ( $n = 162$ )

	TP	Ex-P	Al-P	Fe-P	Oc-P	Ca-P
CC	0.17*	0.05	0.07	0.14	0.09	−0.09
MMC	−0.37**	−0.15	−0.10	−0.28**	−0.23**	0.17*
LOI	0.40**	0.17*	0.09	0.29**	0.25**	−0.17*
TC	0.34**	0.16*	0.14	0.36**	0.14	−0.13
TN	0.42**	0.22**	0.23**	0.45**	0.18*	−0.21**

\*\*Correlation is significant at the 0.01 level (2-tailed)

\*Correlation is significant at the 0.05 level (2-tailed)

seemed that there was no relation of the content variations between Ca-P and TP, for the Ca-P was stable and autogenetic and had little relevance to the eutrophic statuses.

Additionally, strong positive correlations were observed among Ex-P, Al-P and Fe-P of sediments, and the analysis on the various lake areas of correlations of different components or elements show similarly pattern in Fig. S5 (Supplementary Material). Due to the mobile characteristic, these phosphorus fractions were easily desorbed from sediments and released to the overlying water. When the ambient conditions changed, these fractions would be readily to release from sediments, which could be used to estimate the potential release of sediment phosphorus to the overlying water and provide valuable information for the understanding of lake eutrophication [9]. As the results of serious water pollution and intensive human activities, the eutrophication was found in most regions of Taihu Lake [5].

Given that the presence of microcystis was a powerful indicator of lake eutrophication, the contents of microcystis in different sample sites were investigated and the



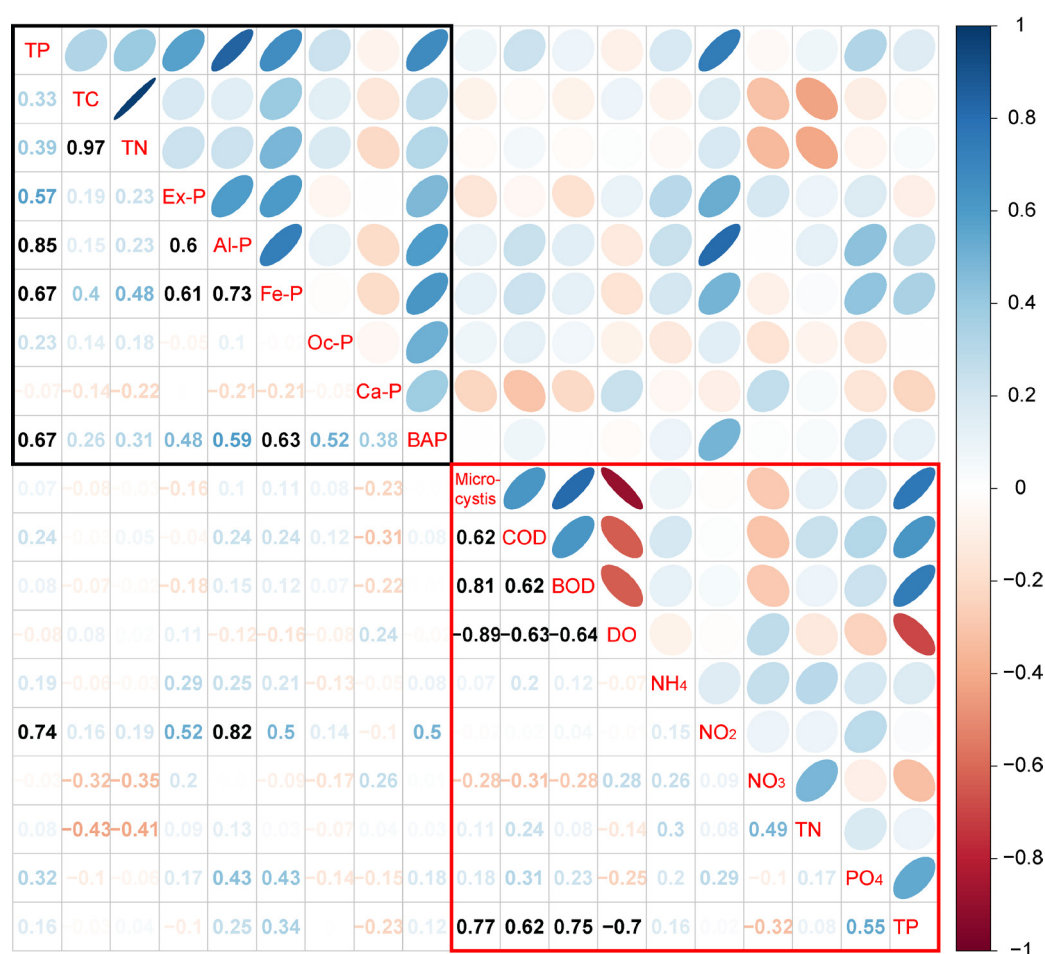


Fig. 6. Correlation analysis of various components or fractions in water or sediments of Taihu Lake. The parameters in sediments and water body were located in black and red box respectively. The coefficient and confidence ellipse were displayed in the top right and bottom left corner respectively, and the coefficient with strong correlations (Pearson coefficient  $\geq 0.6$ ) were shown as bold.

correlation with other values of water and sediments was analysed. It was clear that the concentrations of oxygen demand (COD and BOD) and TP in water showed great positive correlation with the microcystis, which suggested that the eutrophic status was determined by the concentrations of COD, BOD and TP in overlap water. COD and BOD were usually used to assess the degree of organic pollution of water quality, and the contribution to eutrophication was confirmed [34]. The organic matters in water can be degraded accompany with the consumption of DO and proliferation of microorganism, so the variation of BOD determined the evolvement of lake state for it is considered as bio-degradable. Excessive concentrations of P is the most common cause of eutrophication in freshwater lakes, reservoirs, and streams, and soluble orthophosphate (SOP) has considered as the main form of P that autotrophs can assimilate [35]. In the present study, an interesting finding is that the concentration of SOP did not correlate with microcystis growth despite the strong correlation between TP and microcystis bloom. This result suggests that the presence of SOP did not account for eutrophication, and other forms of phosphorus were responsible for the microcystis bloom. Therefore, more attention should be focused

on the different roles of various forms of phosphorus in lake eutrophication.

The eutrophic status of lakes is often accompanied by fluctuation in DO concentrations as well as COD, BOD and TP. Generally, the DO concentrations would decrease sharply when the lake evolved into the mesotrophic stage, and the value of DO would further decline to the lowest value (close to 0) in eutrophic lakes [35,36]. Herein, a strong negative correlation (Pearson coefficient,  $-0.96$ ) was found between DO variation and microcystis growth. Overall, accompany with the lake eutrophication, the concentrations of COD, BOD and TP in water body increased and DO values showed significant decrease.

The potential risk of sediments to overlying water was evaluated in the current study. As is seen in Fig. 6, most parameters in sediments have no significant correlations with the ones of overlying water. For example, the TP of overlying water does not correlate with the TP in sediment as well as the phosphorus of other forms. These results indicate that the majority of P in surface sediments was likely stabilized and did not directly contribute to the internal P loading to the water column. Previous publications proved that sediments and external inputs were two main source of P loading in



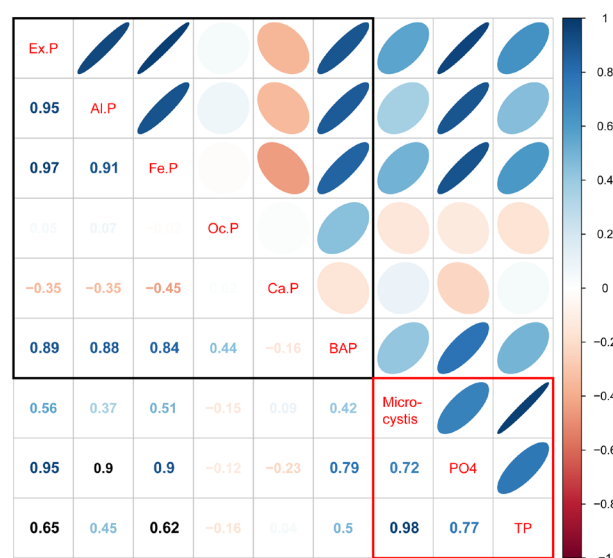


Fig. 7. Correlation analysis of various components or fractions in water or sediments of selected areas in Taihu Lake. The parameters in sediments and water body were located in black and red box respectively.

overlying water, and the contribution of sediment P to the water column was determined by the form of P, environmental factors and the external inputs [2]. In this study, the different environmental conditions such as pH and size distributions of sediments across the lake might attribute to the complexity of sediment-water interface. Therefore, different properties of various areas determined the different patterns.

Furthermore, the correlation analysis in the areas with serious eutrophic status was conducted, such as Zhushan Bay and Lake East Taihu. As can be seen in Fig. 7, the TP in water column has significant positive correlations with Ex-P and Fe-P in sediments, and similar strong correlations are observed between  $\text{PO}_4^{3-}$  of overlying water and Ex-P, Al-P, Fe-P and BAP of sediments. Therefore, in the eutrophic areas, Ex-P and Al-P were readily to exchange between sediments and water, and these fractions of P were the primary component responsible for the P release to water column.

#### 4. Conclusion

In summary, the eutrophic status of Taihu Lake was investigated via the measurements of nutrient elements in surface sediment and other vital parameters (oxygen demand, DO and microcystis growth) in overlying water. The distribution pattern of nutrient elements exhibited significant area-dependent characteristics, namely the concentrations of TC, TN and TP closely associated to the geographical locations, especially the economic pattern of adjacent areas, which resulted in the different types of eutrophication. Through the underlying analysis of various forms of phosphorus, we proved that most of the phosphorus in sediments were present as the bio-unavailable forms, and Fe-P accounted for the primary component of BAP. Subsequently, analyses on intercorrelations among various fractions revealed that microcystis blooms were strongly

correlated to the concentrations of BOD, COD and TP in water, as well as the depletion of DO.

This study highlighted the roles of different element, component and forms in lake eutrophication process, and the correlation analysis provided powerful evidences of internal relations of various forms, elements and eutrophic status of Taihu Lake. Aiming at the differential types of eutrophic state, we should control the key factor to prevent the severe eutrophication. Therefore, in the future research on lake eutrophication, the correlation analysis accompany with component analysis can be adopted for revealing the underlying mechanism from complex system. Further, more studies should be performed on the nutrient mass balance and elements transformation and transportation, including the vertical and horizontal.

#### Acknowledgement

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#### Appendices

Supplementary material is available in the online version of this article, which contains Fig. S1-S5 and Table S1-S2.

#### References

- [1] B. Qin, P. Xu, Q. Wu, L. Luo, Y. Zhang, Environmental issues of lake Taihu, China, *Hydrobiologia*, 581 (2007) 3–14.
- [2] X. Bai, S. Ding, C. Fan, T. Liu, D. Shi, L. Zhang, Organic phosphorus species in surface sediments of a large, shallow, eutrophic lake, Lake Taihu, China, *Environ. Pollut.*, 157 (2009) 2507–2513.
- [3] H. Xu, H.W. Paerl, B. Qin, G. Zhu, G. Gao, Nitrogen and phosphorus inputs control phytoplankton growth in eutrophic Lake Taihu, China, *Limnol. Oceanogr.*, 55 (2010) 420–432.
- [4] T. Zhang, X. Wang, X. Jin, Variations of alkaline phosphatase activity and P fractions in sediments of a shallow Chinese eutrophic lake (Lake Taihu), *Environ. Pollut.*, 150 (2007) 288–294.
- [5] B. Qin, Approaches to mechanisms and control of eutrophication of shallow lakes in the middle and lower reaches of the Yangze river, *J. Lake Sci.*, 14 (2001) 193–202.
- [6] T. Daniel, A. Sharpley, J. Lemunyon, Agricultural phosphorus and eutrophication: A symposium overview, *J. Environ. Qual.*, 27 (1998) 251–257.
- [7] M. Søndergaard, J.P. Jensen, E. Jeppesen, Role of sediment and internal loading of phosphorus in shallow lakes, *Hydrobiologia*, 506 (2003) 135–145.
- [8] P.J. Withers, C. Neal, H.P. Jarvie, D.G. Doody, Agriculture and eutrophication: where do we go from here?, *Sustainability*, 6 (2014) 5853–5875.
- [9] S.L. Xiang, W.B. Zhou, Phosphorus forms and distribution in the sediments of Poyang Lake, China, *Int. J. Sediment Res.*, 26 (2011) 230–238.
- [10] H. Li, Y. Wang, L.Q. Shi, J. Mi, D. Song, X.J. Pan, Distribution and fractions of phosphorus and nitrogen in surface sediments from Dianchi lake, China, *Int. J. Environ. Res.*, 6 (2012) 195–208.
- [11] W.C. An, X.M. Li, Phosphate adsorption characteristics at the sediment-water interface and phosphorus fractions in Nansi Lake, China, and its main inflow rivers, *Environ. Monit. Assess.*, 148 (2009) 173–184.

- [12] S. Powers, T. Burt, N.-I. Chan, J.J. Elser, P.M. Haygarth, N. Howden, H.P. Jarvie, H.M. Peterson, J. Shen, F. Worrall, Legacy phosphorus accumulation and management in the global context: Insights from long-term analysis of major river basins, in: AGU Fall Meeting Abstracts, 2014, pp. 06.
- [13] H.P. Jarvie, A.N. Sharpley, V. Brahana, T. Simmons, A. Price, C. Neal, A.J. Lawlor, D. Sleep, S. Thacker, B.E. Haggard, Phosphorus retention and remobilization along hydrological pathways in karst terrain, *Environ. Sci. Technol.*, 48 (2014) 4860–4868.
- [14] L. Gao, J.M. Zhou, H. Yang, J. Chen, Phosphorus fractions in sediment profiles and their potential contributions to eutrophication in Dianchi Lake, *Environ. Geol.*, 48 (2005) 835–844.
- [15] K.-U. Ulrich, R. Pöthig, Evidence for aluminium precipitation and phosphorus inactivation in acidified watershed-reservoir ecosystems, *Silva Gabreta*, 4 (2000) 185–198.
- [16] E.K. Read, M. Ivancic, P. Hanson, B.J. Cade-Menun, K.D. McMahon, Phosphorus speciation in a eutrophic lake by  $^{31}\text{P}$  NMR spectroscopy, *Water Res.*, 62 (2014) 229–240.
- [17] A. Zhou, D. Wang, H. Tang, Phosphorus fractionation and bio-availability in Taihu Lake (China) sediments, *J. Environ. Sci.*, 17 (2005) 384–388.
- [18] D. Trolle, G. Zhu, D. Hamilton, L. Luo, C. McBride, L. Zhang, The influence of water quality and sediment geochemistry on the horizontal and vertical distribution of phosphorus and nitrogen in sediments of a large, shallow lake, *Hydrobiologia*, 627 (2009) 31–44.
- [19] U. Selig, T. Leipe, W. Dörfler, Paleolimnological records of nutrient and metal profiles in prehistoric, historic and modern sediments of three lakes in north-eastern Germany, *Water, Air, Soil Pollut.*, 184 (2007) 183–194.
- [20] R. Lu, Analytical methods for soils and agricultural chemistry, China Agricultural Science and Technology Press, Beijing (1999) 107–240.
- [21] A.E. Greenburg, L.S. Clesceri, A.D. Eaton, Standard methods for the examination of water and wastewater, Public Health Assoc., Washington, DC (1992).
- [22] W. Zhu, M. Li, Y. Luo, X. Dai, L. Guo, M. Xiao, J. Huang, X. Tan, Vertical distribution of *Microcystis* colony size in Lake Taihu: Its role in algal blooms, *J. Great Lakes Res.*, 40 (2014) 949–955.
- [23] S. Zhai, H. Zhang, Water quantity and waste load variation of rivers around Lake Taihu from 2000 to 2002, *J. Lake Sci.*, 18 (2006) 225–230.
- [24] X. Li, Y. Zhao, Advanced treatment of dyeing wastewater for reuse, *Water Sci. Technol.*, 39 (1999) 249–255.
- [25] J. Sardans, A. Rivas-Ubach, J. Peñuelas, The C: N: P stoichiometry of organisms and ecosystems in a changing world: A review and perspectives, *Perspect. Plant Ecol. Evol. Syst.*, 14 (2012) 33–47.
- [26] P. Tett, M. Droop, S. Heaney, The Redfield ratio and phytoplankton growth rate, *J. Mar. Biol. Assoc. U.K.*, 65 (1985) 487–504.
- [27] A. Kaiserli, D. Voutsas, C. Samara, Phosphorus fractionation in lake sediments - Lakes Volvi and Koronia, N. Greece, *Chemosphere*, 46 (2002) 1147–1155.
- [28] P. Wang, M.C. He, C.Y. Lin, B. Men, R.M. Liu, X.C. Quan, Z.F. Yang, Phosphorus distribution in the estuarine sediments of the Daliao river, China, *Estuar. Coast. Shelf S.*, 84 (2009) 246–252.
- [29] Q. Zhou, C. Gibson, Y. Zhu, Evaluation of phosphorus bioavailability in sediments of three contrasting lakes in China and the UK, *Chemosphere*, 42 (2001) 221–225.
- [30] A. Kisand, P. Nöges, Sediment phosphorus release in phytoplankton dominated versus macrophyte dominated shallow lakes: importance of oxygen conditions, *Hydrobiologia*, 506 (2003) 129–133.
- [31] T. Gonsiorczyk, P. Casper, R. Koschel, Phosphorus-binding forms in the sediment of an oligotrophic and an eutrophic hardwater lake of the Baltic Lake District (Germany), *Water Sci. Technol.*, 37 (1998) 51–58.
- [32] X. Jin, S. Wang, Y. Pang, H. Zhao, X. Zhou, The adsorption of phosphate on different trophic lake sediments, *Colloid Surf. A-Physicochem. Eng. Asp.*, 254 (2005) 241–248.
- [33] M.R. Penn, T. Auer, E.L. Van Orman, J.J. Korienek, Phosphorus diagenesis in lake sediments: investigations using fractionation techniques, *Mar. Freshwater Res.*, 46 (1995) 89–99.
- [34] Q. Guo, X. Wang, X. Han, J. Wang, Spatial distribution of COD and its contribution to the eutrophication in Bohai Sea, *Mar. Sci.*, 29 (2005) 71–75.
- [35] D.L. Correll, The role of phosphorus in the eutrophication of receiving waters: A review, *J. Environ. Qual.*, 27 (1998) 261–266.
- [36] R.E. Hecky, The eutrophication of Lake Victoria, *Proc. International Association of Theoretical and Applied Limnology*, 25 (1993) 39–39.

Supplementary Material



Fig. S1. The pictures illustrating the eutrophic status of Taihu Lake in 2007 (from Google Image).

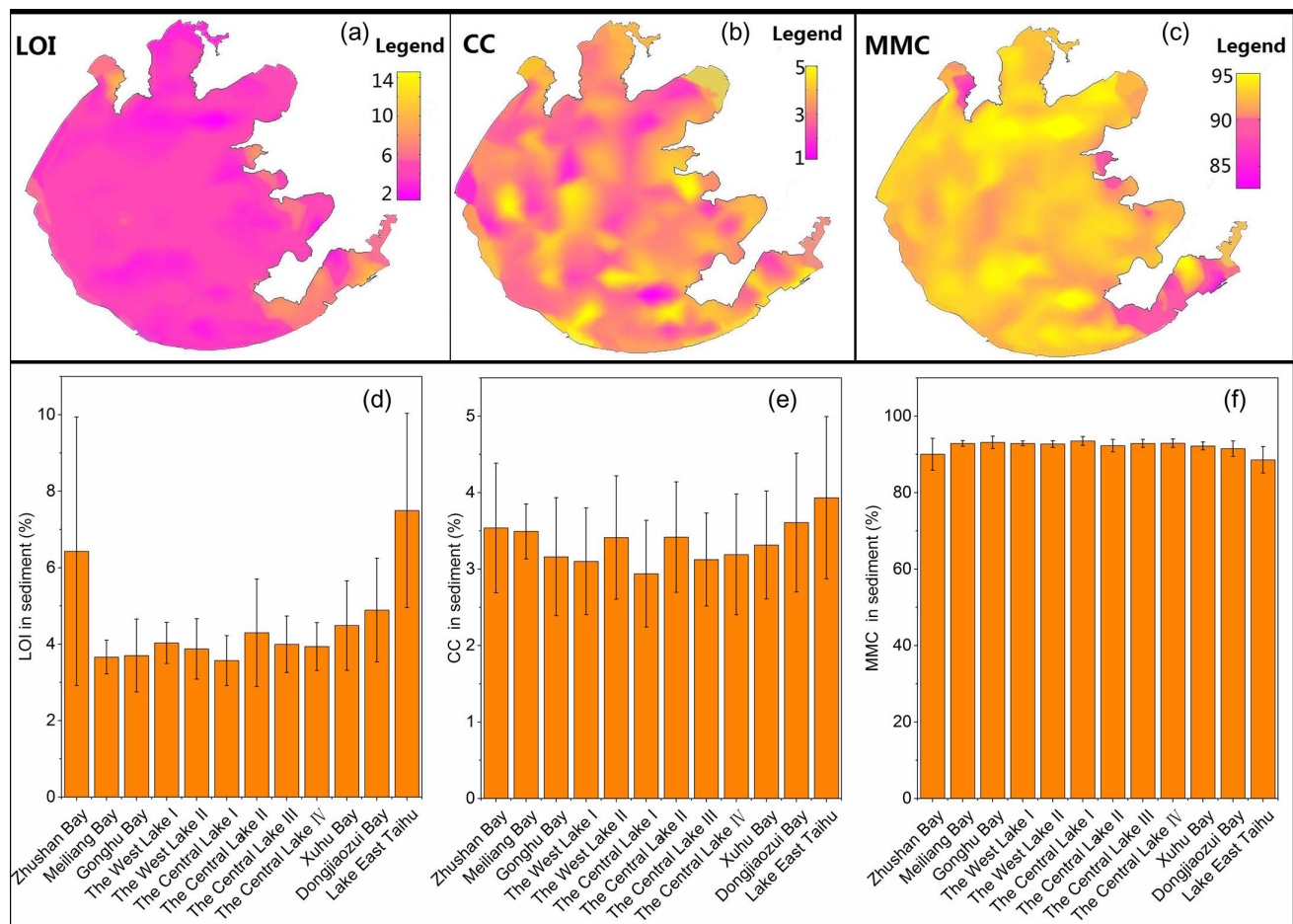


Fig. S2. The spatial distributions of LOI (a), CC (b) and MMC (c) in surface sediment of Taihu Lake, China; the percent of LOI (d), CC (e) and MMC (f) in different regions.



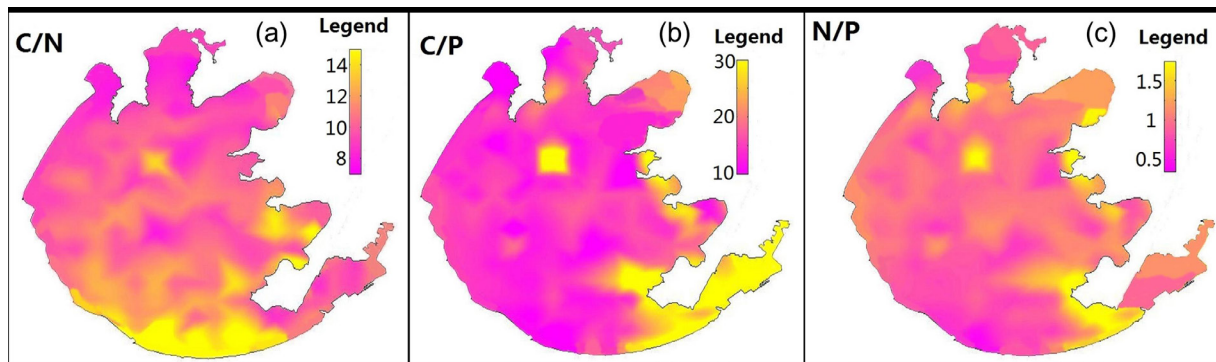


Fig. S3. Spatial distribution of the ratios of C, N and P in surface sediments of Taihu Lake.

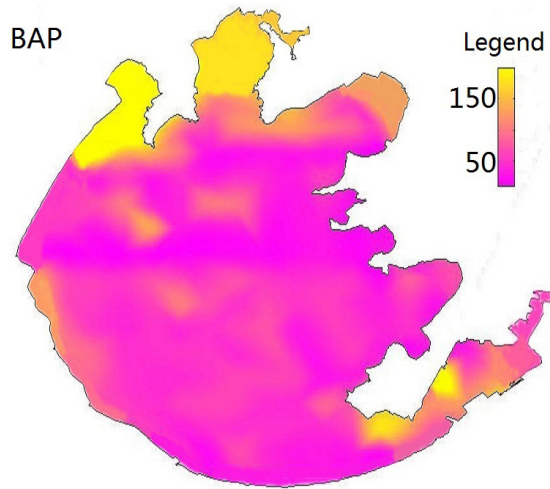


Fig. S4. The spatial distribution of BAP (bio-available) in surface sediment of Taihu lake.

Table S1  
Physical and chemical parameters of overlying water

Parameters	pH	DO (mg/L)	TN (mg/g)	TP (mg/g)
Min	7.12	0.21	0.49	0.01
Max	8.04	1.91	4.32	0.36
Mean	7.35	1.13	2.30	0.05

Table S2  
Physical and chemical parameters of sediment

Parameters	pH	water ratio (%)	grain size (mm)	clay (%)	slit (%)	sand (%)
Min	7.69	31.5	0.006	5.21	68.46	11.07
Max	8.27	60.8	1.941	9.18	83.86	28.16
Mean	8.11	55.4	0.018	7.10	76.24	19.65

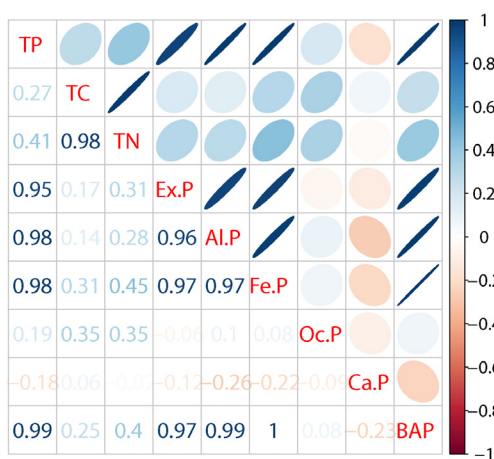


Fig. S5. Correlation analysis of various components or fractions in sediments of different lake areas in Taihu Lake.