Environmental Science and Pollution Research (2019) 26:22295–22304
https://doi.org/10.1007/s11356-019-05489-0

RESEARCH ARTICLE

Distribution characteristics and pollution risk evaluation of the nitrogen and phosphorus species in the sediments of Lake Erhai, Southwest China

Xiong Pan[1,2] · Li Lin[1,2] · Zhuo Huang[1,2] · Min Liu[1,2] · Lei Dong[1,2] · Jin Chen[2,3] · John Crittenden[4]

Received: 31 October 2018 / Accepted: 14 May 2019 / Published online: 31 May 2019

Abstract
Erhai is a famous tectonic rift lake in China. In this study, the distribution of nitrogen and phosphorus species in Erhai sediment cores and their ecology risk were evaluated. The total nitrogen (TN) in the sediment cores ranged from 1583.3 to 8018.5 mg/kg. Nitrogen (N) was still accumulating in the sediment. For depths of 0 to 25 cm, the TN decreased dramatically and for deeper depths the TN got stabilized. The proportions of various N fractions in the sediments of the study areas ranked as follows: the strong oxidation extractable N (SOEF-N) > the weak acid extractable N (WAEF-N) > the strong alkali extractable N (SAEF-N) > the ion-exchangeable N (IEF-N). The total phosphorus (TP) ranged from 814.9 to 1442.3 mg/kg. The vertical distribution of each fraction of phosphorus showed that there were different sources of sediment phosphorus around the Erhai Lake. The results of nitrogen and phosphorus pollution evaluation in sediments by single pollution standard index method showed that the standard index of the TN (S_{TN}) ranged from 4.29 to 14.01, and the standard index of the TP (S_{TP}) ranged from 1.69 to 2.18. It illustrated that N and P in the sediments were the serious ecological pollution risks in Erhai Lake.

Keywords Erhai Lake · Sediment · Nitrogen forms · Phosphorus forms · Vertical distribution · Risk assessment

Introduction

The eutrophication of lakes has been a hot environmental science topic in China since 1970 (Li et al. 2012). Research on the water quality in the past decades has shown a significant decline in water quality and is due to human activities in Erhai Lake's watershed. Erhai is currently in a transition from a mesotrophic lake to a eutrophic lake (Wang et al. 2015). Among the reasons, increases in N and P in the lake have played two key roles for this transition (Wang et al. 2015; Aranguren-Riaño et al. 2018). Moreover, releases of N and P from the sediment could increase the N and P in the water column, which in turn impacts the aquatic ecosystem (Wang et al. 2008; Li et al. 2012). Accordingly, determination of the N and P species in the sediment are always useful to determine their release from the sediment and cycling between the water column and sediments and their impact on eutrophication (Gardner et al. 1995; Tang et al. 2018a, b).

Studies have demonstrated that sediment always acts not only as a sink of nutrients but also as a source (Aigars and Carman 2001). The accumulation of N and P in the sediment could increase the primary productivity of the lake (Elser et al. 2007; Li et al. 2016). And the phytoplankton could be limited with the releasing of endogenous nitrogen and phosphorus by a N to P ratio of water lower than 44.2 (Elser et al. 2009; Zhang et al. 2018). Usually, when the environmental

Responsible editor: Philippe Garrigues

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s11356-019-05489-0) contains supplementary material, which is available to authorized users.

✉ Li Lin
linli1229@hotmail.com

[1] Basin Water Environmental Research Department, Changjiang River Scientific Research Institute, Wuhan 430010, Hubei, China

[2] Key Lab of Basin Water Resource and Eco-Environmental Science in Hubei Province, Wuhan 430010, Hubei, China

[3] Administration office, Changjiang River Scientific Research Institute, Wuhan 430010, Hubei, China

[4] Brook Byers Institute of Sustainable Systems, School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

conditions are changed, the deposition of endogenous N and P will respond and change correspondingly. Under the combined influence of microorganisms and other physical and chemical effects, such as mineralization and ion exchange, the sediment N will eventually be released and exist in a dissolved (Yu et al. 2016; Tang et al. 2018a, b). In sediment interstitial water, N will transfer from the sediment to the overlying water and re-involve in the nitrogen biogeochemical processes (Yang et al. 2017a, b).

Not all forms of N and P in the sediments can be released to the overlying water. For example, organic complexes of P cannot usually escape from the sediment, but others, such as iron, calcium, and aluminum salts, can escape from the sediments (Wang et al. 2009). Loosely sorbed P (Ex-p) can be released immediately. Different P fractions are measured using different sequential extraction schemes in sediments (Ruban et al. 1999; Li and Huang 2010). In previous studies, sediment nitrogen has always been simply divided into inorganic N and organic N. The transformation and release probability of organic N has been used to evaluate their contribution to eutrophication levels (Aigars and Carman 2001). However, now we usually use the terms transferable and non-transferable N fractions using an improved P fractional extraction method. Transferable N could be further separated into four fractions, including the ion-exchangeable form (IEF-N), the weak acid extractable form (WAEF-N), the strong alkali extractable form (SAEF-N), and the strong oxidation extractable form (SOEF-N) (Li et al. 2012). IEF-N is the nitrogen form most easily released, followed by WAEF-N, SAEF-N, and SOEF-N in terms of transferable N (Lv et al. 2005a; Wang et al. 2015). Ni et al. (2016) points out that current lake eutrophication control strategies are associated with major deficiencies due to lack of clear understanding of nutrient biogeochemical characteristics. These operational definitions help to understand the migration and transformation nitrogen. The relevant research helps to understand the nutrient biogeochemical characteristics.

Erhai Lake is mainly polluted by agricultural non-point source. The water quality entered into Erhai is grade V or worse than grade V, while the discharging one is grade II or III (Jiao et al. 2013; Xiang et al. 2016). How does the change of water quality affect the enrichment of nitrogen in the sediment of Erhai Lake? No studies have revealed it. On the other hand, Erhai Lake has been under unprecedented governance, especially in the last 5 years (Ji et al. 2017; Zhao et al. 2017). The environmental governance experience of Erhai is well worth studying. Keep abreast of distribution characteristics of the N and P species in the sediments is a basic requirement for the summary of environmental governance experience. But there is no research on it after the pollution supervision and control in Erhai Lake basin.

The objective of this study was to simultaneously investigate the latest distribution characteristics of the N and P species in the sediments of Erhai Lake with the same batch of samples along the flow direction in the central section. Previously, there was poor knowledge about N and P species and their potential release to the overlying water, and no knowledge about how the change of water quality affected the enrichment of nitrogen in the sediment. For those purposes, we used sequential extraction schemes to measure the N and P species in Erhai sediments. Nitrogen was defined in four forms: IEF-N, WAEF-N, SAEF-N, and SOEF-N. Phosphorus was defined as four forms: Ex-P, Al/Fe-P, RS-P, and Ca-P. Accordingly, our study developed a better understanding on the evolution of sediment N and P loading and ecological risk and offered guidance for controlling the release of N and P in Erhai Lake next.

Materials and methods

Study area

Erhai (N 25° 36′–25° 58′, E 100° 06′–100° 18′), the seventh largest freshwater lake in China and the second largest lake in Yunnan Province, is a typical tectonic rift lake that sits within a north-south-oriented inter-mountain basin at an altitude of 1974 m (Ni et al. 2016; Yang et al. 2017a, b). With the swift development of agriculture in the drainage basin, the water quality of Erhai Lake has been deteriorating daily and the presence of N and P from agricultural runoff has increased primary productivity. As a result, the lake has transitioned from being a mesotrophic lake to a eutrophic lake. The catchment area is 2565 km^2; the lake area is 252.1 km^2, and the reservoir capacity is 2.96 billion m^3 (Li et al. 2016). The maximum depth of Erhai Lake is 21.3 m, and the average depth is 10.8 m. The basin has jurisdiction over 16 towns, 167 village committees, and 33 communities. At the end of 2014, the total population of the Erhai basin is 844,700.

According to the date from the Chinese Academy of Environmental Sciences, the vegetation occupied 50.36% of the catchment area, while the forest coverage rate was 37.0% (http://www.dali.gov.cn/dlzwz/5117496551576436736/20160802/309260.html). Agriculture and tourism of the basin are primarily concentrated in the western and southeastern lowland plain regions. The southern lakeside is a scenic tourist city, while the eastern is low mountainous area (Yang 2016). It is known as the “mother lake” for the people of Dali city. Erhai Lake supplies Dali city not only the primary water source for drinking but also for recreation, industrial, and agricultural production. In addition, it plays a key role in regulating the climate of Dali, promoting the agricultural development of the whole river basin, even the economic sustainable development.

Sample collection

We divided Erhai Lake into three areas, including northern, middle, and southern regions. With the help of the Erhai water depth contour map, we chose five sampling points after factoring in the hydrological characteristics and sediment pollution levels of Erhai Lake. The five sampling points along the flow direction of Erhai Lake in the central section were numbered 1 to 5, respectively. The northernmost one was an estuary of the Mizu River, which was the primary water source for Erhai Lake. In addition, the southernmost one was the only natural lake outlet. A 40-cm length of columnar sediment was sampled from each site using a sediment corer and equally divided into eight sections in June 2018. The sampling locations were shown in Fig. 1. In addition, samples of the overlying water were also collected in each session.

All the sediment samples were stored in sterile and sealable plastic bags and placed in a refrigerator (4 °C) at the laboratory. Before the experiment, the samples were freeze dried, ground, and homogenized through a 100-mesh screen.

Sediment analysis

The TN in sediment was measured using the Kjeldahl method as previously described (Bremner and Mulvaney 1982). The

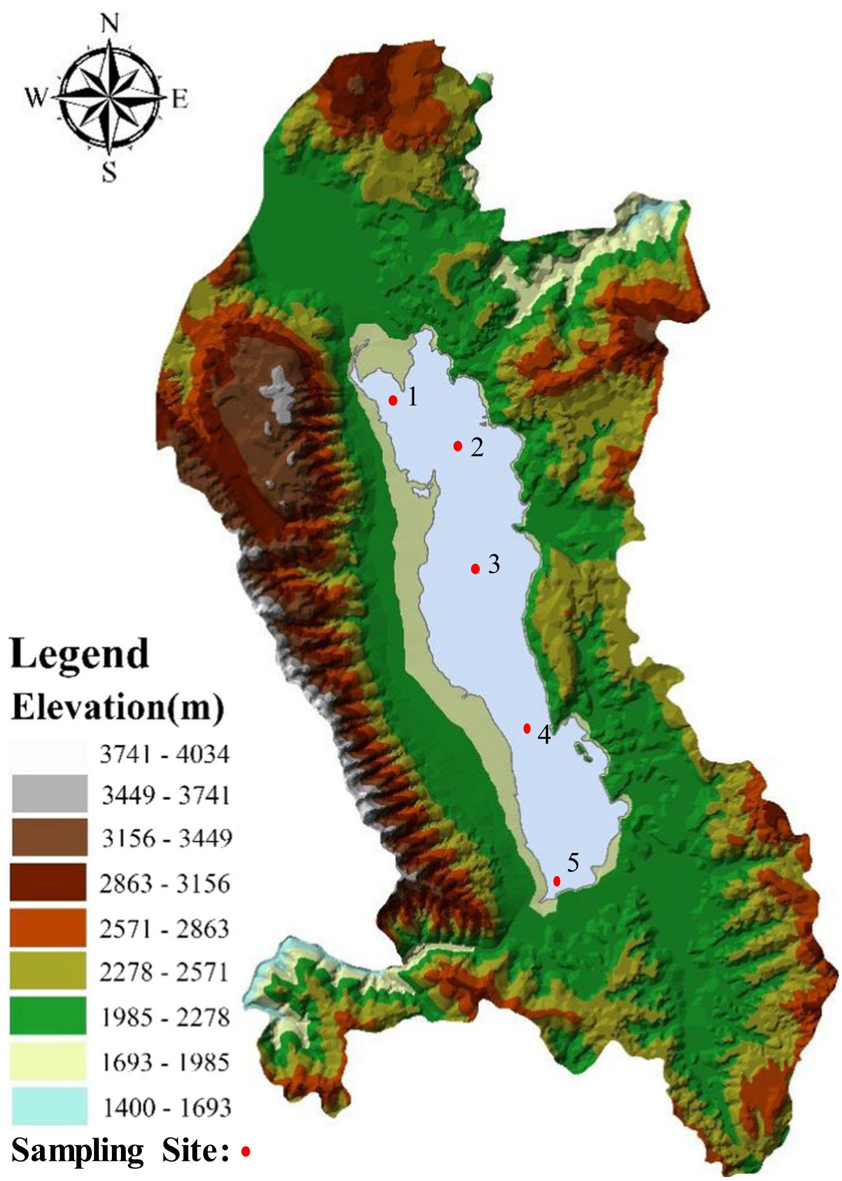

Fig. 1 Sampling sites of the sediments in Erhai Lake

total transferable nitrogen (TTN) of these samples was also investigated at the same time as described by Song and Ma (2002). This nitrogen fractionation method used the phosphorus fraction method described by Ruttenberg (1992) with some modifications. The TTN primarily consists of IEF-N, WAEF-N, SAEF-N, and SOEF-N. In addition, the extraction procedure of these four forms of nitrogen was sequential with 1 M MgCl, HAc-NaAc (pH = 5), 0.1 M NaOH, and $K_2S_2O_8$ (alkaline) as described by Tang et al. (2018a). The extracts were centrifuged, and N concentration was determined with spectrophotometer (Wang et al. 2008).

The TP content in the sediment was analyzed using the standard measurement and testing protocol (Ruban et al. 1999). The various phosphorus species were sequentially extracted as described by Tang et al. (2018b) with 1 M NH_4Cl, 0.1 M $NaHCO_3$-NaS_2O_3, 1 M NaOH, and 0.5 M HCl, respectively. In this method, the inorganic phosphorus (IP) fractions would be divided into exchangeable or loosely sorbed phosphorus (Ex-P), aluminum- or iron-bound phosphorus (Al/Fe-P), reductant-soluble phosphorus (RS-P), and calcium-bound phosphorus (Ca-P). The analysis of phosphorus in each extracting solution was conducted using the molybdenum blue method (GB3838-2002) (MEP 2002). All the instruments used sediment sample analysis had passed national measurement examination. And the reference materials (GSD-9) and standard reagents were used for quality control. Set one parallel for every five samples.

Eco-risk assessment methods

The guide issued by the Environment and Energy Ministry of Ontario, Canada was used to assess the nitrogen and phosphorus pollution risk of the Erhai sediments (Leivuori and Niemistö 1995). The guide used a standard index for each contaminant *i* using the following equation:

$$S_\mathrm{i} = C_\mathrm{i}/C_\mathrm{s} \tag{1}$$

$$\mathrm{FF} = \sqrt{\frac{F^2 + F_{\max}^2}{2}} \tag{2}$$

where S_i was a single evaluation index or standard index, and if $S_\mathrm{i} > 1$ this indicated that the contaminant concentrations exceeds the standard value. C_i was the measured concentration of contaminant *i* (g/kg). C_s was the standard value of contaminant *i* (g/kg). FF was the comprehensive pollution index. F was the average of all the pollution indices (the average of S_{TN} and S_{TP}). F_{max} was the maximum single pollution index (the maximum of S_{TN} and S_{TP}). The minimum levels of TN and TP that could cause the ecological risk were 550 and 600 mg/kg, respectively.

Data processing

The raw data was processed using Microsoft Excel 2010 (Microsoft, Redmond, Washington, USA). The analysis of variance (ANOVA) was conducted to determine the significance of difference using the SPSS software package (SPSS 19.0 for Windows, USA). The scattergram was prepared using Origin 8.0 (Origin Lab Corporation, Northampton, MA, USA).

Results and discussion

Recovery evaluation

Recovery experiments were performed to ensure the dependability of the nitrogen and phosphorus extraction method in certified reference material (GSD-9). The obtained recovery of TN was 98.13% with a relative standard deviation of less than 3.57%. The obtained recovery of TP was 95.29% with a relative standard deviation of less than 2.76% (Table S1). The results indicated that the recovery processes were satisfactory for the experimental requirements for the determination of the N and P.

Total nitrogen in the sediments

The TN in the sediments and overlying water parameters were presented in Fig. 2 and Table S2, respectively. It ranged from 1583.3 to 8018.5 mg/kg, and No. 5 and No. 3 samples are dramatically higher near the surface of the sediment. All results exceeded 1000 mg/kg which was the Chinese environmental protection and EPA standard (EPA 2002; Wang et al. 2010). The standard was a level where the sediments should be dredged to protect the environment. With increasing depth of sediment, the TN content basically decreased. These

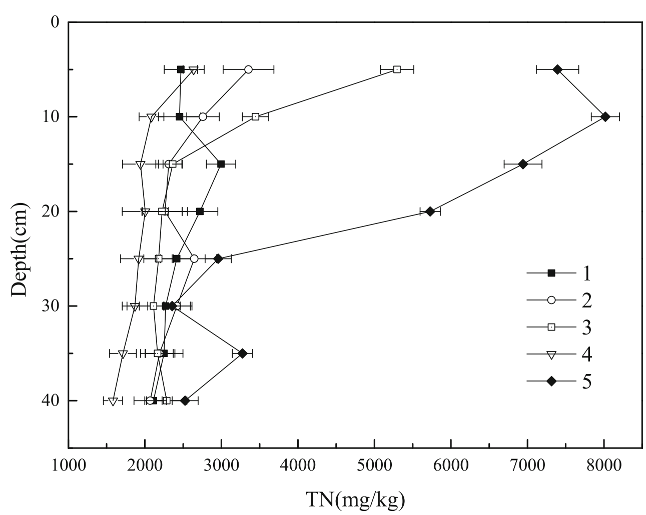

Fig. 2 Concentrations of TN at various depths in Erhai sediments

relative TN concentrations were similar to other freshwater lake sediment studies (Yang et al. 2017a, b). Within the range of 0–25 cm, the decrease in the TN content was rapid as the depth increased, and it stabilized below 25 cm. The southern area of Erhai showed the highest TN average concentration of the sediments, followed by the northern area and the central areas. In contrast, Zhao et al. (2013a) reported that the spatial distribution of TN in the Erhai surface sediments was similar to that in the northern area and was higher than the southern area followed by the central area. It might be the reason that the economic development of the southern urban areas had increased nitrogen emissions over the previous years. Along the flow direction of Erhai Lake, north to south, TN and TDN contents of the overwater at the sampling points showed an opposite distribution when compared with their sediments TN contents (shown in Table 1). It indicated that N might be still accumulating in Erhai sediment. Similar to the results, Wang et al. (2015) emphasized that Erhai was currently in a transition from Mesotrophic Lake to a Eutrophic Lake.

Currently, Erhai is a mesotrophic lake. However, the TN concentration in Erhai sediments are close to or even higher than the eutrophic lakes in the middle and lower reaches of the Yangtze River area, such as Taihu and Chaohu Lakes (Wang et al. 2008, 2010). Similar results were reported in Dianchi Lake, another famous plateau lake in Yunnan province, whose TN concentration of surface sediments ranged from 1775.4 to 22,384.1 mg/kg (Li et al. 2012). The reason might be that they were located at high altitudes, and both were close to a large city where most of the domestic and industrial sewage had not been adequately treated and was directly discharged into the lake (Li et al. 2012). Similar to the results, Catalan and Donato Rondón (2016) emphasized that human settlement and farming could lead to potential eutrophication in mountain lakes at elevations that were less impacted by watershed development at temperate latitudes. As shown in Fig. 2, sampling point No. 5, which was adjacent to the downtown area of Dali City and might be also polluted by domestic and industrial sewage that directly discharged into the lake, contained the highest TN content. For the No. 3 sampling point, the sediment had a lower temperature and less flow disturbance caused because the water depth was 18.2 m. These were the reasons why we found high concentrations of TN at No. 3 point where less nitrogen was released (shown in Table S2) (Yu et al. 2016; Yang et al. 2017a, b).

Table 1 The overwater quality of Erhai Lake (mg/L)

Sample	TN	TP	TDN	TDP
NO.1	2.90	0.26	0.67	0.03
NO.2	0.64	0.16	0.55	0.02
NO.3	0.55	0.12	0.52	0.02
NO.4	0.40	0.10	0.37	0.02
NO.5	0.47	0.10	0.42	0.03

TDN, total dissolved nitrogen; *TDP*, total dissolved phosphorus

Total phosphorus in the sediments

The TP concentrations at various depths of the sediments are presented in Fig. 3, which ranged from 814.9 to 1442.3 mg/kg. The TP concentration decreased as a whole with increasing depth. Similar vertical distribution features were reported in other various freshwater lake sediments, such as Taihu and Dianchi Lakes (Zhang et al. 2007; Yang et al. 2017a, b; An and Li 2009), but the P sediment concentrations in most Chinese lake sediments were seldom above 750 mg/kg. However, the TP sediment concentrations in this study were obviously higher than that. In addition, it was even higher than in the famous eutrophic lakes, such as Taihu Lake in China, where the TP concentration was under 1000 mg/kg in most regions (Zhang et al. 2007). However, in similar study on the Dianchi Lake, the P concentration reached 3200 mg/kg (Yang et al. 2017a, b). Yang et al. 2017a, b showed that high concentration of sediment P concentration was due to the application of large amounts of phosphorus fertilizers. The high content of TP at the No. 3 sampling point might be due to the same reason. The farmland around the No. 3 sampling point was primarily used for garlic cultivation and higher phosphorus fertilizers applications were used. Lago de Tota in the Andean was also a high mountain lake. Aranguren-Riaño et al. 2018 studied the carbon and nitrogen stable isotopic signatures of invertebrates in this lake and pointed out onion agriculture in the watershed contributed the bulk of nutrients supporting elevated productivity in Lago de Tota.

Nitrogen fractions in the sediments

To estimate potential nitrogen release, the vertical distributions of the IEF-N, WAEF-N, SAEF-N, and SOEF-N contents

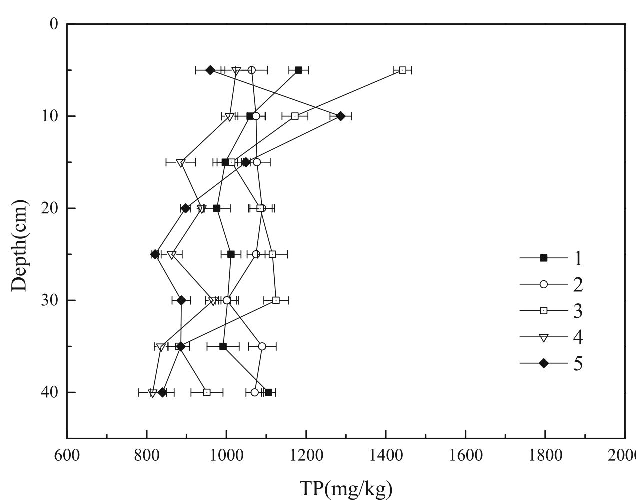

Fig. 3 Concentrations of TP at various depths in Erhai sediments

were measured, and the results were shown in Fig. 4a–d. The concentrations of IEF-N were between 16.1 and 166.0 mg/kg. The average concentration of IEF-N was 67.5 mg/kg. The relative content and variation trend of IEF-N at each sample point were consistent with their TN content (Fig. 4a). In addition, the estimated value of the IEF-N was significantly greater than that reported in the estuaries of Dianchi Lake (Yang et al. 2017a, b). Some TN values even reached the level of the Yangtze River area (Wang et al. 2008). As the IEF-N was very easily released into the overlying water (Lv et al. 2005a), Barik et al. (2016) stated that IEF-N was extremely likely to participate in the N cycle of the lake through the interaction between the sediments and interstitial water. Their retention and release participated in the seasonal variation of the N pool in sediments. Therefore, the study of IEF-N in Erhai sediments indicated the risk of endogenous nitrogen pollution.

The WAEF-N form is relatively sensitive to the pH value as the name implies. When the environment became acidic, the WAEF-N would release N and participate in the N cycle of the sediments (Lv et al. 2005b; Zhang et al. 2016). As shown in Fig. 4b, the WAEF-N content ranged from 311.9 to 446.3 mg/kg. It gradually decreased with the increasing depth of the sediment. The trend was also consistent with the TN and IEF-N contents. The maximum value appeared at the southern exit of the lake (No. 5 sample point), and the minimum value appeared in the northern entrance of the lake (No. 1 sample point). The average concentration of WAEF-N in Erhai was 370.2 mg/kg. However, the risk of the WAEF-N fraction release from the sediment would not be very high considering that the pH of the Erhai Lake water was slightly alkaline as shown in Table 2. In addition, Wang et al. (2014) reported that WAEF-N could convert to SOEF-N through microbial mineralization.

SAEF-N was a nitrogen form, which was sensitive to the redox environment and bound to ferromanganese (Zhao et al. 2013a). As shown in Fig. 4c, the SAEF-N content ranged from 81.7 to 431.6 mg/kg. The average concentration of the SAEF-N in Erhai was 183.1 mg/kg. The maximum value appeared at the No. 5 sample point. SOEF-N primarily referred to the nitrogen form, which was combined with organic matter and sulfide (Zhao et al. 2013a). As shown in Fig. 4d, the SOEF-N content ranged from 1191.2 to 1548.2 mg/kg. The average concentration of SOEF-N in Erhai was 1337.6 mg/kg. Compared with IEF-N and WAEF-N, the SOEF-N was more difficult to release (Yang et al. 2017a, b). Lv et al. (2005a), suggesting that the total benthos biomass had a positive relationship with SOEF-N in the sediment and the organic-binding nitrogen was easily

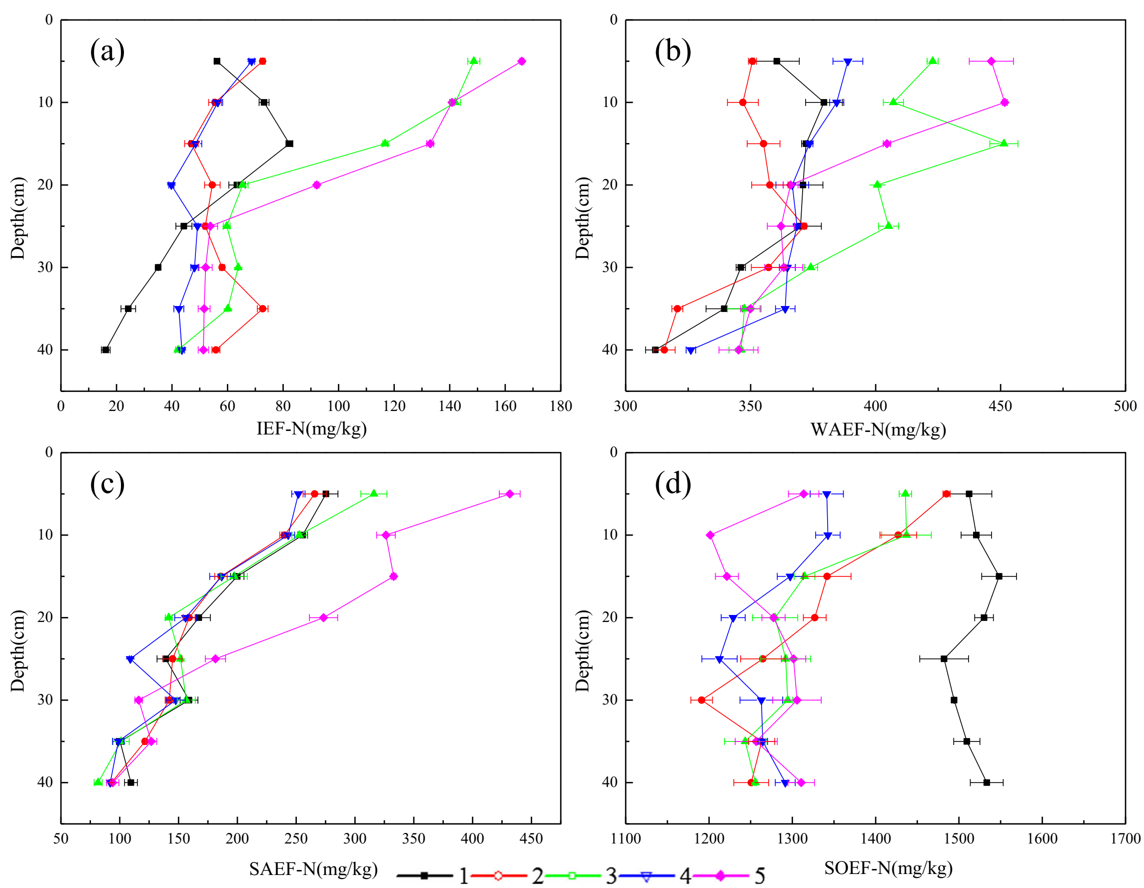

Fig. 4 Concentrations of **a** ion-exchangeable form (IEF-N), **b** weak acid extractable form (WAEF-N), **c** strong alkali extractable form (SAEF-N), and **d** strong oxidation extractable form (SOEF-N) for various sediment depths

Table 2 Comprehensive pollution risk assessment for the surface sediments in Erhai Lake

Sample	S_{TN}	S_{TP}	FF
No. 1	3.84–5.45 (4.47)	1.63–1.97 (1.74)	3.38–3.91 (3.85)
No. 2	3.76–6.10 (4.55)	1.67–1.82 (1.78)	3.31–5.13 (3.92)
No. 3	3.84–9.63 (5.02)	1.47–2.40 (1.89)	3.37–8.03 (4.31)
No. 4	2.88–4.79 (3.58)	1.36–1.78 (1.55)	2.52–4.09 (3.11)
No. 5	4.29–14.58 (8.91)	0.83–2.14 (1.51)	3.65–11.88 (7.30)

Date in parentheses means the averages

utilized by the benthos biomass. This research indicated that microorganisms were active under environments with high concentrations of SOEF-N.

Overall, the proportions of the various N fractions in the sediments of the study areas ranked as follows: SOEF-N > WAEF-N > SAEF-N > IEF-N. Wang et al. (2008) indicated that the rank in the middle and lower Yangtze river was as follows: SOEF-N > IEF-N > WAEF-N > SAEF-N. Therefore, the IEF-N was relatively small in the sediments of Erhai Lake. IEF-N is the primary nitrogen form exchanged at the sediment-water interface. This study indicated that the nitrogen release amount of the sediments of Erhai Lake was small, but the mass fraction and proportion of bioavailable nitrogen, such as WAEF-N was high. Thus, the nitrogen release risk of the Erhai Lake sediments was relatively high.

Phosphorus fractions in the sediments

To determine the potential release of phosphorus in the Erhai sediments, the vertical distributions of the Ex-P, Al/Fe-P, RS-P, and Ca-P concentrations for various depths were measured and shown in Fig. 5a–d. The concentrations of Ex-P were between 4.7 and 43.8 mg/kg. The average concentration of Ex-P was 11.1 mg kg^{-1}. Ex-P is a phosphorus form that was very easily released to the overlying water in the sediment (Ruban et al. 1999). As shown in Fig. 5, the Ex-P concentration in the Erhai sediments accounted for only 0.4–4.6% of the TP content, which was the lowest among the four phosphorus forms. This average proportion was lower than that found in Chaohu Lake (4.3%) and similar to that in Dianchi Lake (0.1–3.5%) (Jiao et al. 2018; Yang et al. 2018). It was relatively high of depth of 0 to 10 cm and was stabilized for deeper depth. The obvious difference at the No. 5 sampling point might be caused by phosphate adsorption by the aquatic macrophytes (Yang et al. 2018).

Al/Fe-P is another form of phosphorus that can be more easily released and has a significant correlation with the total phosphorus content in pore water (Wang et al. 2012). It had the highest fraction among the four phosphorus forms. The concentrations were between 360.7 mg/kg and 537.5 mg/kg, and the average concentration was 451.9 mg/kg. As shown in Fig. 5, Al/Fe-P both increased gradually with depth and then remained stable. This trend was consistent with a previous study on Erhai Lake (Zhao et al. 2013b). Al/Fe-P was particularly abundant at the lake entrance (No. 1) and low in the center of the lake (No. 3). However, the TP concentration at the No. 3 sampling point was the highest. This shows that there were different sources of sediment phosphorus from the catchment basin around Erhai Lake (Jiao et al. 2018).

RS-P was primarily affected by the redox of the water environment. The content in Erhai Lake was between 52.2 and 365.5 mg kg^{-1} (Fig. 5c). Overall, RS-P tended to decrease with the increasing depth. The reason may be that decreases in the DO promoted the release of RS-P from the sediments. Erhai Lake was a permanent aerobic lake with little change in redox potential (Xiang and Zhou 2010). Thus, very little RS-P would be released little at this point. The Ca-P content ranged from 175.6 to 375.6 mg/kg. It tended to increase with the depth increase. Ni and Wang (2015) pointed out that Ca-P was unavailable to algae, and the content was largely dependent on the lake position and naturally occurring background calcium levels in the soils within the watershed. It also explained why the content of Ca-P did not change as much with depth as the other forms of phosphorus content at the majority of the sampling sites.

Pollution risk of nitrogen and phosphorus from the sediments

A comprehensive pollution assessment for the surface sediments in Erhai Lake was conducted. The detailed assessment results are shown in Table 2. The standard index of the TN (S_{TN}) in the surface sediments ranged from 2.88 to 14.58. The standard index of TP (S_{TP}) in the surface sediments ranged from 0.83 to 2.40. The comprehensive pollution index (FF) in the surface sediments ranged from 2.52 to 11.88. After making a comparison with the comprehensive pollution assessment standard for the Environment and Energy Ministry of Ontario, Canada methods (shown in Table 3), all the surface sediments were at level 4 of pollution which illustrated the heavy contamination by nitrogen and phosphorus. The Environment and Energy Ministry of Ontario Canada had also emphasized that the total nitrogen concentration of sediment with serious ecological risk effect was 4800 mg/kg (Leivuori and Niemistö 1995). However, the highest content of TN in the Erhai sediment at NO.3 and NO.5 sampling point both were exceed this standard value. This result ensured the serious ecological pollution risk of Erhai Lake again. Lake Baikal is the deepest lake in the world and has no releasing risk of nitrogen and phosphorus from its sediments. During the same period, TN of Baikal sediments was 1630 mg/kg at most which was far less than that in Erhai (Semenov et al. 2018). Similar to the results of this study, Zhao et al. (2013a) pointed out TN of Erhai sediments ranged from 2354 to 6174 mg/kg

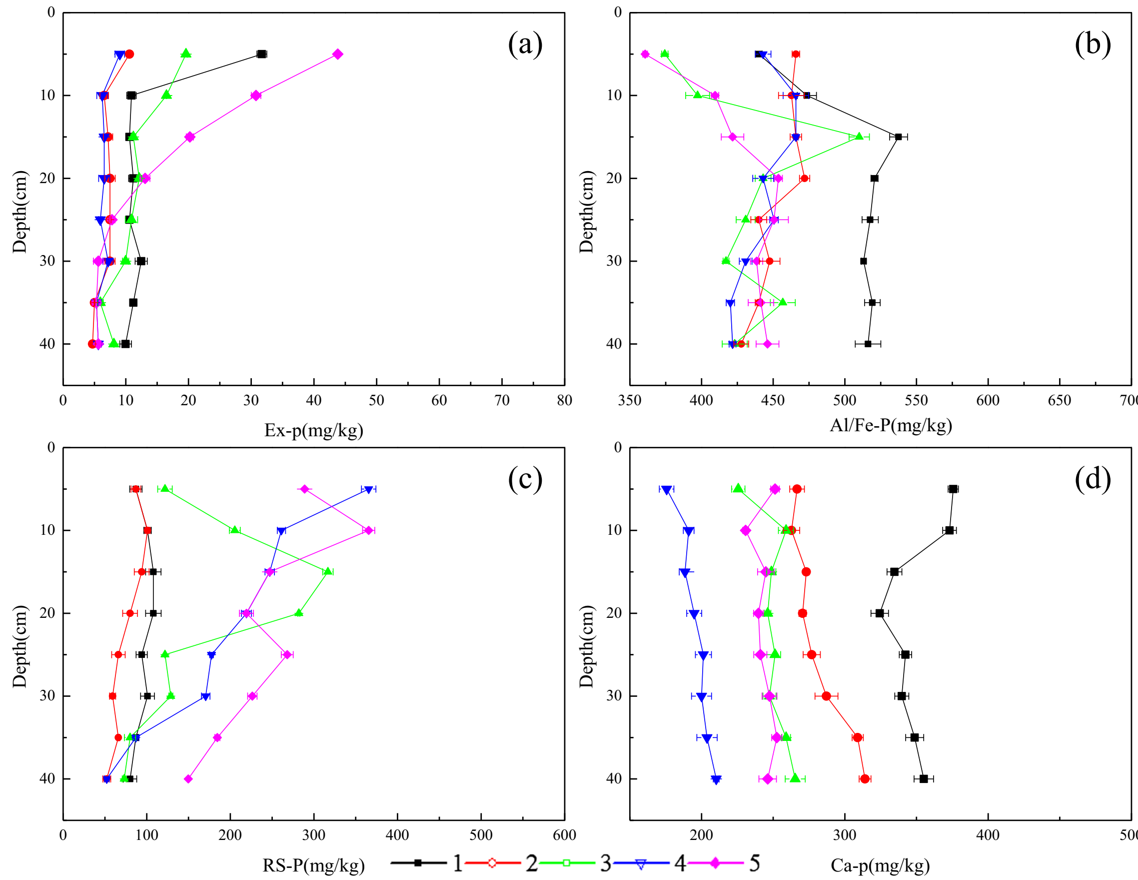

Fig. 5 Concentrations of **a** exchangeable or loosely-sorbedphosphorus (Ex-P), **b** aluminum- or iron-bound phosphorus (Al/Fe-P), **c** reductant-soluble phosphorus (RS-P), and **d** calcium-bound phosphorus (Ca-P) for various sediment depths

and jugged the great nitrogen releasing risk clear for the same Lake. But they had not given a comprehensive pollution assessment in combination with nitrogen and phosphorus. Five years later, the overall pollution risk in Erhai is still rising.

Conclusions

This study investigated the fractions, vertical distribution, and ecological risks of nitrogen and phosphorus in the Erhai sediments. After a comprehensive analysis and discussion of the results, some conclusions could be drawn as follows:

(1) The contents of TN in the Erhai sediments were close to or even higher than those in eutrophic lakes in the middle and lower reaches of the Yangtze River area. The southern area showed the highest average TN concentration, followed by the northern and central areas. It indicated that the economic development of the southern urban areas had increased nitrogen emissions over the previous years. And N might still be accumulating in Erhai sediment.

(2) The proportions of various N fractions in the sediments of the study areas ranked as follows: SOEF-N > WAEF-N > SAEF-N > IEF-N. IEF-N was the primary nitrogen form exchanged at the sediment-water interface.

Table 3 Standard and level of comprehensive pollution assessment for the methods issued by the Environment and Energy Ministry of Ontario, Canada

Level	S_{TN}	S_{TP}	FF	Comment
1	$S_{TN} < 1.0$	$S_{TP} < 0.5$	FF < 1.0	Clean
2	$1.0 \le S_{TN} \le 1.5$	$0.5 \le S_{TP} \le 1.0$	1.0 ≤ FF ≤ 1.5	Mild pollution
3	$1.5 < S_{TN} \le 2.0$	$1.0 < S_{TP} \le 1.5$	1.5 < FF ≤ 2.0	Middle pollution
4	$S_{TN} > 2.0$	$S_{TP} > 1.5$	FF > 2.0	Heavy pollution

Although the content of IEF-N was relatively low in the sediments, the mass fraction and proportion of bioavailable nitrogen (WAEF-N) were high. Thus, the nitrogen release risk of the Erhai Lake sediments was relatively high.

(3) The levels of TP in Erhai sediment were obviously higher than those in most Chinese lake sediments, even the famous eutrophic lakes such as Taihu Lake in China. The vertical distribution of each fraction of phosphorus (Ex-P, Al/Fe-P, RS-P, and Ca-P) indicated that there were different sources of sediment phosphorus for Erhai Lake.

Funding This study was supported by the State-level Public Welfare Scientific Research Institutes Basic Scientific Research Business Project of China (No.CKSF2019433/SZ, NO.CKSF2019380SH, No. CKSF2017062/SH), and the Strategic Priority Research Program of the Chinese Academy of Sciences (XDA23040303). Also, the authors gratefully acknowledge the support from the Brook Byers Institute for Sustainable Systems, Hightower Chair and the Georgia Research Alliance at the Georgia Institute of Technology.

References

Aigars J, Carman R (2001) Seasonal and spatial variations of carbon and nitrogen distribution in the surface sediments of the gulf of Riga, Baltic Sea. Chemosphere 43(3):313–320

An WC, Li XM (2009) Phosphate adsorption characteristics at the sediment–water interface and phosphorus fractions in Nansi Lake, China, and its main inflow rivers. Environ Monit Asse 148(1–4): 173–184

Aranguren-Riaño NJ, Shurin JB, Pedroza-Ramos A, Muñoz-López CL, López R, Cely O (2018) Sources of nutrients behind recent eutrophication of Lago de Tota, a high mountain Andean lake. Aquat Sci 80(4):39–48

Barik SK, Bramha SN, Mohanty AK, Bastia TK, Behera D, Rath P (2016) Sequential extraction of different forms of phosphorus in the surface sediments of Chilika lake. Arab J Geosci 9(2):1–12

Bremner JM, Mulvaney CS (1982) Nitrogen—total. In: Page AL, Miller RH, Keeney DR (eds) Methods of soil analysis. Part 2. Chemical and microbiological properties, 2nd edn. Soil Science Society of America, Inc. and American Society of Agronomy, Inc., Madison, pp 595–624

Catalan J, Donato Rondón JC (2016) Perspectives for an integrated understanding of tropical and temperate high-mountain lakes. J Limnol 75:215–234

Elser JJ, Bracken ME, Cleland EE, Gruner DS, Harpole WS, Hillebrand H (2007) Global analysis of nitrogen and phosphorus limitation of primary producers in freshwater, marine and terrestrial ecosystems. Ecol Lett 10(12):1135–1142

Elser JJ, Andersen T, Baron JS, Bergström AK, Jansson M, Kyle M, Nydick KR, Steger L, Hessen DO (2009) Shifts in lake N:P stoichiometry and nutrient limitation driven by atmospheric nitrogen deposition. Science 326(5954):835–837

EPA (2002) A guidance manual to support the assessment of contaminated sediments in freshwater ecosystems. EPA, USA

Gardner WS, Cavaletto JF, Johengen TH, Johnson JR, Heath RT, Cotner JB Jr (1995) Effects of the zebra mussel, dreissena polymorpha, on community nitrogen dynamics in Saginaw bay, Lake Huron. J Great Lakes Res 21(4):529–544

Ji NN, Wang SR, Zhang L (2017) Characteristics of dissolved organic phosphorus inputs to freshwater lakes: a case study of lake Erhai, Southwest China. Sci Total Environ 601-602:1544–1555

Jiao LX, Zhao HC, Wang SR (2013) Temporal and spatial distribution of nitrogen and phosphorus in water body of Erhai Lake and effect on concentration of chlorophyll-a. Res Environ Sci (In Chinese) 26(5): 527–533

Jiao Y, Yang C, He W, Liu WX, Xu FL (2018) The spatial distribution of phosphorus and their correlations in surface sediments and pore water in Lake Chaohu, China. Environ Sci Pollut Res Int 25(1):1–10

Leivuori M, Niemistö L (1995) Sedimentation of trace metals in the Gulf of Bothnia. Chemosphere 31(8):3839–3856

Li DP, Huang Y (2010) Sedimentary phosphorus fractions and bioavailability as influenced by repeated sediment resuspension. Ecol Eng 36(7):958–962

Li H, Wang Y, Shi LQ, Mi J, Song D, Pan XJ (2012) Distribution and fractions of phosphorus and nitrogen in surface sediments from Dianchi lake, China. Int J Environ Res 6(1):195–208

Li Y, Xie P, Zhao DD, Zhu TS, Guo LG, Zhang J (2016) Eutrophication strengthens the response of zooplankton to temperature changes in a high-altitude lake. Ecol Evol 6(18):6690–6701

Lv XX, Song JM, Yuan HM, Li XG, Zhang TR, Li N, Gao XL (2005a) Geochemical characteristics of nitrogen in different grain size sediment from the southern Huanghai Sea. Acta Oceanol Sin 27(1):64–69

Lv XX, Song JM, Yuan HM, Li XG, Zhang TR, Li N, Gao XL (2005b) Geochemical characteristics of nitrogen in the southern Yellow Sea surface sediments. J Marine Syst 56(1–2):17–27

MEP, P.R.C (Ministry of Environmental Protection of the People's Republic of China) 2002 Environmental quality standards for drinking water (GB3838-2002), Beijing (in Chinese)

Ni ZK, Wang SR (2015) Economic development influences on sediment-bound nitrogen and phosphorus accumulation of lakes in China. Environ Sci Pollut Res 22(23):18561–18573

Ni ZK, Wang SR, Wang YM (2016) Characteristics of bioavailable organic phosphorus in sediment and its contribution to lake eutrophication in China. Environ Pollut 219:537–544

Ruban V, Lópezsánchez JF, Pardo P, Rauret G, Muntau H, Quevauviller P (1999) Selection and evaluation of sequential extraction procedures for the determination of phosphorus forms in lake sediment. J Environ Monitor 1(1):51–66

Ruttenberg KC (1992) Development of a sequential extraction method for different forms of phosphorus in marine sediments. Limnol Oceanogr 37(7):1460–1482

Semenov MY, Marinaite II, Zhuchenko NA, Silaev AV, Vershinin KE, Semenov YM (2018) Revealing the factors affecting occurrence and distribution of polycyclic aromatic hydrocarbons in water and sediments of Lake Baikal and its tributaries. Chem Eco 34(10):925–940

Song J, Ma H (2002) Nitrogen forms and decomposition of organic carbon in the southern Bohai Sea core sediments. Acta Oceanol Sin 21(1):125–133

Tang Y, Li M, Xu D, Huang J, Sun J (2018a) Application potential of aerobic denitrifiers coupled with a biostimulant for nitrogen removal from urban river sediment. Environ Sci Pollut Res 25(6):1–14

Tang XQ, Wu M, Li R (2018b) Phosphorus distribution and bioavailability dynamics in the mainstream water and surface sediment of the Three Gorges Reservoir between 2003 and 2010. Water Res 145: 321–332

Wang SR, Jin X, Jiao L, Wu F (2008) Nitrogen fractions and release in the sediments from the shallow lakes in the middle and lower reaches of the Yangtze River area, China. Water Air Soil Poll 187(1–4):5–14

Wang P, He M, Lin C, Men B, Liu R, Quan X, Yang Z (2009) Phosphorus distribution in the estuarine sediments of the Daliao river, China. Estuar Coast Shelf Sci 84(2):246–252

Wang SH, Jiang X, Zhong LX, Jin XC, Sun SQ (2010) Seasonal occurrence characteristics of different forms of nitrogen in the sediments of Chaohu Lake. Environ Sci 31(4):946–953

Wang S, Jiao LX, Yang S, Jin X, Yi W (2012) Effects of organic matter and submerged macrophytes on variations of alkaline phosphatase activity and phosphorus fractions in lake sediment. J Environ Manage 113:355–360

Wang M, Liu Y, Zheng B, Zhou J, Jiang Q (2014) Nitrogen forms in surface sediments of urban river and their influence factors: a case study of Qingyi river in Xuchang City. China Environ Sci 34(3): 720–726

Wang SR, Zheng B, Chen C, Dohmann M, Kolditz O (2015) Thematic issue: water of the Erhai and Dianchi lakes. Environ Earth Sci 74(5): 3685–3688

Xiang SL, Zhou WB (2010) Phosphorus existing forms and distribution characteristic in lake Poyang sediments. J Lake Sci 22(5):649–654

Xiang S, Pang Y, Chu ZS, Hu XZ, Sun L, Xue LQ (2016) Response of inflow water quality to land use pattern in northern watershed of lake Erhai. J Environ Sci (In Chinese) 37(8):2947–2956

Yang H (2016) Analysis of water quality situation and changer from 2005 to 2014 in Erhai lake. Water Resour Inform 1:25–28

Yang G, Li Z, Fan C (2017a) The effect of ecological rehabilitation of the Erhai lakeside on Odonata species richness and abundance. Aquat Insect 38(4):231–238

Yang WQ, Xiao H, Li Y, Miao DR (2017b) Vertical distribution and release characteristics of nitrogen fractions in sediments in the estuaries of Dianchi Lake, China. Chem Speciat Bioavailab 29(1):110–119

Yang WQ, Xiao H, Li Y, Miao DR (2018) Vertical distribution and release characteristics of phosphorus forms in the sediments from the river inflow area of Dianchi Lake, China. Chem Speciat Bioavailab 30(1): 14–22

Yu J, Fan C, Zhong J, Zhang Y, Wang C, Zhang L (2016) Evaluation of in situ simulated dredging to reduce internal nitrogen flux across the sediment-water interface in lake Taihu, China. Environ Pollut 214: 866–877

Zhang T, Wang X, Jin X (2007) Variations of alkaline phosphatase activity and P fractions in sediments of a shallow Chinese eutrophic Lake (Lake Taihu). Environ Pollut 150(2):288–294

Zhang B, Xu C, Wang S, Wei C (2016) Distribution and bioavailability of nitrogen and phosphorus fractions in street dusts of mega-city, Chendu, Southwest China. Fresenius Environ Bull 25(2):453–463

Zhang Y, Song C, Ji L, Liu Y, Xiao J, Cao X (2018) Cause and effect of N/P ratio decline with eutrophication aggravation in shallow lakes. Sci Total Environ 627:1294–1302

Zhao HC, Wang SR, Jiao LX, Huang D (2013a) Characteristics of temporal and spatial distribution of the nitrogen forms in the sediments of Erhai Lake. Res Environ Sci (In Chinese) 26(3):235–242

Zhao HC, Wang SR, Jiao LX, Huang D (2013b) Characteristics of temporal and spatial distribution of different forms of phosphorus in the sediments of Erhai Lake. Res Environ Sci (In Chinese) 26(3):227–234

Zhao HC, Zhang L, Wang SR, Jiao L (2017) Features and influencing factors of nitrogen and phosphorus diffusive fluxes at the sediment-water interface of Erhai Lake. Environ Sci Pollut Res 25(2):1–10