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RESEARCH ARTICLE

Economic development influences on sediment-bound nitrogen and phosphorus accumulation of lakes in China

Zhaokui Ni[1,2,3] · Shengrui Wang[1,2,3]

Abstract China has been confronted with serious water quality deterioration concurrent with rapid socioeconomic progress during the past 40 years. Consequently, knowledge about economic growth and lake water quality dynamics is important to understand eutrophication processes. Objectives were to (i) reconstruct historical nutrient accumulation and the basin economic progress on burial flux (BF); (ii) determine forms and structures of nitrogen (N) and phosphorus (P) in sediment and water using six cores in three of the most severely eutrophic lake areas in China (i.e., Eastern Plain, Yunnan-Guizhou Plain, and Inner Mongolia–Xinjiang regions). Results suggest that BFs of total nitrogen (TN) continued to increase in sediment, whereas total phosphorus (TP) levels were consistent or only slightly increased, except in highly polluted lakes during the past decades. Similar results were observed for concentrations of nutrients in water (i.e., increased N/P). This historical distribution pattern was correlated to long-term fertilization practices of farmers in the watershed (N fertilization exceeds that of P) and was contingent upon pollution control policies (e.g., emphasized P whereas N was ignored). Vertical profiles of BFs indicated that lake nutrient accumulation included

✉ Shengrui Wang
   wangsr@craes.org.cn

1 State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China

2 State Environmental Protection Key Laboratory for Lake Pollution Control, Research Center of Lake Environment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China

3 Dongting Lake Ecological Observation and Research Station, Yueyang 414000, China

three stages in China. Nutrient accumulation started in the 1980s, accelerated from the 1990s, and then declined after 2000. Before the 1980s, nutrients were relatively low and stable, with nutrient inputs being controlled by natural processes. Thereafter, N- and P-bound sediments dramatically increased due to the increasing influence of anthropogenic processes. Nutrients were primarily derived from industries and domestic sewage. After 2000, BFs of nutrients were steady and even decreased, owing to implementation of watershed load reduction policies. The decreasing NaOH-extracted P (Fe/Al–P) and increasing organic phosphorus (OP) indicated that the source of exogenous pollution underwent a shift. Inputs of nutrients were predominantly from agricultural and domestic sewage, whereas industrial pollution has been gradually controlled in most of the watersheds. Historical nutrient dynamics suggest that the economy of China is growing at the expense of its aquatic ecological environments. Therefore, more attention to nutrient export to groundwater resulting from economic development is important for further aquatic ecosystem deterioration and eutrophication in China.

Keywords Sediments · Nutrient accumulation · Economic progress · China

Introduction

An extraordinary change in global lake ecosystems has occurred over the last 40 years (Liu et al. 2014) from excessive nitrogen–phosphorus loading, which has threatened the health of aquatic ecosystems (Carpenter 2005; Conley et al. 2009). Worldwide monitoring indicates that the incidence of freshwater eutrophication in Asia, Europe, America, and Africa has reached 54, 53, 46, and 28 %, respectively (Nyenje et al. 2010). Nutrient loading in most lakes worldwide has been

controlled by natural processes dating back to the 1960s. However, nutrients have slowly increased in freshwater systems owing to rapid economic development and population increases since that time. As a result, the increased nutrients have caused water quality and aquatic ecosystem deterioration, as well as accelerated eutrophication. Furthermore, such nutrient dynamic alterations have intensified the worldwide ecosystem crisis (Fabricius 2005, Liu et al. 2010).

China is currently the largest and fastest-growing discharger of sewage worldwide, with total sewage discharge increasing from 31 to 69 billion tons (i.e., 121 % increases) from the 1980s to 2013 (Wu et al. 2011). Accordingly, the eutrophic lake area has increased from 135 to 8700 km^2 (i.e., 60-fold increase). Moreover, the area of lakes that are approaching eutrophication (e.g., total nitrogen (TN), total phosphorus (TP), and chlorophyll a concentration reaching 0.2, 0.01, and 10,000 mg·L^{-1}, respectively) has reached 1.4×10^4 km^2, which makes China the highest nutrient loader in freshwater systems (Wang 2015). By 2030, the gross domestic product (GDP) of China is expected to double, which means that lake eutrophication may continually increase. The Chinese State Council and various local governments have conducted a series of load reduction projects and have issued a series of 5-year plans since the mid-1980s to face this challenge (Xu et al. 2011). A sum of US$500 billion has been invested to reduce watershed nutrients loading and restore the damage of aquatic ecosystems (Ministry of Environmental Protection of China (MEP) 2012a). To date, no significant reductions in eutrophication rates have been achieved, despite the considerable financial investment. Therefore, understanding nutrient dynamics due to rapid economic progress has become a major issue among environmental groups, scientists, and policy makers in China.

China's landscape is covered with lakes, as there are more than 2700 lakes with the single area of more than 1 km^2 (total area of about 9×10^4 km^2) (Yang et al. 2010). In addition, there are tens of thousands of artificial lakes and reservoirs, with dozens more under construction. Sediment particles depositing the lake floor are continuously covered by successive sediment layers, thereby preserving valuable historical information about past conditions of watersheds (Zhang and Shan 2008). Correlating influences of economic and social developments on nutrients sediment retention at the national level could provide a better understanding of lake eutrophication mechanisms. Hence, we collected six sediment cores from three of the most severely eutrophic areas in China (i.e., the Eastern Plain, Yunnan-Guizhou Plain, and the Inner Mongolia–Xinjiang regions) to achieve the following objectives: (i) reconstruct historical accumulation of nutrients and (ii) to evaluate the basin economic progress on burial flux (BF) and forms of nitrogen (N) and phosphorus (P) in the sediment, as well as evaluate nutrient structure (i.e., N/P) in the water.

Materials and methods

Study area and background

This study was conducted in the Eastern Plain, Inner Mongolia–Xinjiang, and Yungui Plain regions. Sampling locations and basic properties of lakes and basin are provided in Table 1. The Eastern Plain Lake is the most seriously eutrophic region and the most economically developed area in China. Taihu Lake, Chaohu Lake, and Yanghe reservoir were selected as case studies in this region. Taihu Lake in the Jiangsu Province is the second largest freshwater lake in China. Its basin covers 0.4 % of the total territory of the country, but contributes 10 % of the GDP. As a result, the lake has suffered serious eutrophication. Chaohu Lake in the middle of Anhui Province is the fifth largest freshwater lake in the Yangtze floodplain of China. It not only provides drinking water for the surrounding population, but also plays an important role in the fishery industry. Due to excessive nutrient loading from agricultural, domestic, and industrial sewage, the lake has also experienced severe eutrophication since 1970 (Chen et al. 2013).

The Yanghe reservoir in the northern Hebei Province is one of the medium-to-large water conservancy projects in Northern China. Nutrient inputs are primarily from agricultural intensification and monitoring indicates that agricultural NPS pollution accounts for 72 % of N and 75 % of P loading in this reservoir (Ni et al. 2015). This intensification has caused serious eutrophication and water quality deterioration since the mid-1980s.

The Inner Mongolia–Xinjiang Lake region is an economically underdeveloped area; however, the lakes are suffering from eutrophication (Zhang et al. 2011). Ulansuhai Lake, west of the Inner Mongolia Autonomous region, is a typical agricultural watershed in the upper reaches of the Yellow River in northern China.

The Yungui Plain Lake region is the least economically developed area but has the greatest eutrophication risk (Ni et al. 2011). Dianchi and Erhai Lakes were selected in this area. Dianchi Lake is the largest shallow lake in the Yunnan-Guizhou plateau and the sixth largest one in China. It is also the municipal water source for the nearby Kuming municipal area, the capital of Yunnan Province. Due to rapid economic development and urban expansion in the watershed, the lake has been experiencing cyanobacterial bloom during the last two decades (Liu et al. 2014). Erhai Lake in the western Yunnan Province is one of the largest lakes in China, and plays an important role in local socioeconomic development, including irrigation, drinking water, and tourism. Since the onset of agricultural policies during the early 1980s, a high load of external nutrients have entered the lake, resulting in dramatic deterioration of water quality (from mesotrophic to eutrophic).

Table 1 Summary of basic background along the lakes in different lakes of China

Site	Water area km²	Basin area km²	Depth m	Rainfall mm	Population km²	GDP per capita US$ (2012)	GDP per area billion US$ (2012)	Status
Taihu Lake (E1)	2250	36,500	2.9	1000–1200	1360	7, 499	4.4	Eutrophication
Chaohu Lake (E2)	2063	12,938	1.9	1000–1158	785	5, 216	3.5	Eutrophication
Yanghe reservoir (E3)	14	755	5.7	800–1000	301	4, 841	3.2	Eutrophication
Ulansuhai Lake (M)	293	12,000	1.5	450–600	27	5, 303	0.13	Eutrophication
Dianchi Lake (Y1)	330	2920	5	950–1100	980	7010	5	Eutrophication
Erhai Lake (Y2)	250	2565	10.2	1000–1200	333	3, 862	1.3	Mesotrophy

Sediment sampling

Six sediment cores (E1, E2, E3, M, Y1, and Y2) were collected at different lakes using a core sampler (HL-CN, Hengling technology Ltd., Corp., China) to a depth of 35 cm in November 2010. Core E1 (120° 11′ 29″ E, 31° 30′ 46″ N) was located in Meiliang Bay of Taihu and Core E2 (117° 36′ 09.29″ E, 31° 33′ 41.51 N) being located East of the Chao Lake. Core E3 (119° 12′ 30.20″ E, 39° 59′ 45.30″ N) was located in the central Yanghe Reservoir. Core M (108° 49′ 17″ E, 40° 53′ 54″ N) was located at the center of Ulansuhai Lake. Core Y1 (102° 38′ 34.54″ E, 24° 59′ 30.50″ N) was located in central Dianchi Lake. Core Y2 (100° 14′ 5.35 E, 25° 41′ 24.91 N) was located in the underwater platform of south Erhai. Generally, these selected cores had more stable sedimentary environments and were less affected by human activity than the other areas, so the cores more reliably reflect the real nutrient deposition situation.

Immediately after collection, sediment cores were divided into 2-cm slices in sequence, stored in the dark at 4 °C, and then were freeze-dried (Ni et al. 2015). Samples were mixed using the quartering method, with a portion used for porosity and dry density analysis, and the other portion passed through a 100-mesh sieve after grinding and used for TN, TP, and organic matter (OM), as well as for determinations of N and P forms.

Analytical procedures

TN, TP, and OM

TN content was measured in accordance with the semi-micro Kjeldahl method (Jin et al. 1990) and by using standard measurements and testing protocol (Ruban et al. 1999). Organic matter was measured by using the dichromate external heating method (Nanjing institute of soil, Chinese Academy of Science 1978).

BFs

BF is essential to determine the amount of buried biogenic elements in sediments and its influencing factors. The formula for BF is as follows (Schenau et al. 2005):

$$BF = c\ \omega\rho_d = cS(1-\varphi)\rho_d,$$

Where BF is the burial flux of biogenic elements, $g \cdot (cm^2 \cdot year)^{-1}$; c is the content of biogenic elements, $mg \cdot kg^{-1}$; ω is the mass deposition rate of the sediments, $g \cdot (cm^2 \cdot year)^{-1}$; S is the deposition rate, $cm \cdot year^{-1}$, φ denotes porosity, %; and ρ_d is the dry density of the sediments, $g \cdot cm^{-1}$.

Porosity and dry density of sediments were measured using a fully automatic vacuum density analyzer (3H-2000TD1, Beishide Instrument Technology (Beijing) Co., Ltd.). Deposition rate was determined via sediment ^{137}Cs and ^{210}Pb dating. The deposition rates of different cores in this study were obtained from previous studies (Ni 2011; Ni et al. 2011; Yao and Li 2004; Zhang 2013; Zhang et al. 1993, Zhang et al. 2005). Previous studies showed that the deposition rates in core E1, E2, E3, M, Y1, and Y2 were 0.32, 0.27, 0.62, 0.95, 0.28, and 0.20 $cm \cdot yr^{-1}$, respectively.

N forms

N forms contain inorganic-N and organic-N (Org-N). Inorganic-N includes NH_4^+–N, NO_3^-–N, and NO_2^-–N. NO_2^-–N is ignored in this study because of the content of NO_2–N in sediments from all locations was low and almost zero. Sediment NH_4^+–N was analyzed via the KCl extraction–brilliant cresyl blue colorimetric method (Sun et al. 2006), and the NO_3^-–N was analyzed by the phenol disulfonic acid spectrophotometry method. Because the Kjeldahl digestion method for determining TN did not include NO_3^-–N and NO_2^-–N, the content of Org-N could be roughly defined as the difference between TN and NH_4^+–N.

P forms

P forms were analyzed by using the standard measurement test procedure (Ruban et al. 1999). P forms were divided into organic P, NaOH-extracted P (Fe/Al–P), and HCl-extracted P (Ca–P).

Quality assurance and control

Data quality was controlled using field duplicate and spiked samples, standard reference materials, and method blanks. The analysis procedure was controlled under the same conditions. The procedure was repeated twice for each sample. The relative percent difference in the duplicate samples was <6 %.

Results

Temporal distribution of BFs

The BFs of TN and TP were compared to the sample age of six selected cores to reconstruct the environmental history and determine impacts of natural and anthropogenic activities on lakes throughout China's industrialization from the past several decades (Fig. 1). Vertical profiles of BFs of TN exhibited an increasing trend, whereas the historical BFs of TP were not synchronous with TN except for core E3. Generally, vertical variation of TN and TP BFs in sediment from the six cores mainly included three stages:

Stage I (i.e., prior to the 1980s) showed that the BFs of nutrients in different cores had the lowest levels throughout all profiles. The BFs of TN from different cores had the least difference and maintained a steady trend with a mean value of 681 mg·(m^2·year)$^{-1}$. The BFs of TP had considerable difference in cores because of the large differences in their pollution status of P and lake position during this stage. The mean value of BFs of TP was 432 mg·(m^2·year)$^{-1}$.

Stage II (i.e., early 1980s to 2000) indicated that BFs of TN had increasing trends with an average increase of 156 % for cores. The increasing rate of BFs in severely polluted lakes

suggested further loading. This was primarily attributed to increases in exogenous N loading in watersheds. The BFs of TP presented a slight to no increase except for E2 and M.

Stage III (i.e., after 2000) demonstrated that the BFs of TN in sediments had a relatively high value but the increasing trend gradually stabilized. The BFs of TP exhibited a decreasing trend excluding that of E3.

Temporal distribution and partition of N

The content of TN and N forms versus sample age of the six cores are presented in Fig. 2. The sequence of TN content in sediments was Y2 > Y1 > E3 > E1 > E2 > M, with an average of 2236, 1697, 1337, 1139, 1007, and 957 mg·kg^{-1}, respectively. The mean content of TN in sediments from Yungui Plateau was the highest, followed by that from the Eastern Plain, and then from the Mountain Mongolia–Xinjiang lakes. The result is consistent with that from Li et al. (2010) in that, an obvious inflection point also appeared during the 1980s (except in E1 and Y1). The content of TN was the lowest and kept steady before this inflection. Thereafter, it increased dramatically, with average increases of 330 % since 1980s. The content of TN in core E1 and Y1 began increasing in the 1950s, with rates augmented by the 1980s, in conjunction with human population.

Sediment N was included with organic-N and inorganic-N. Organic-N, representing the non-labile N in sediment (Jones and Willett 2006), was the dominant N form in the sediment cores (accounting for 85–97 % of TN). The content of organic-N sequence in the cores exhibited a similar trend with TN (i.e., Y2 > Y1 > E3 > E1 > E2 > M) and with an average of 2092, 1570, 1271, 969, 966, and 902 mg·kg^{-1}, respectively. Historical distribution of organic-N was similar to that of the TN.

NH$_4^+$–N that represents labile inorganic-N in sediment, was primarily derived from the ammonification of organic-N and human activities. The distribution was mainly affected by microbial activity, organic-N mineralization, aquatic plant, and sediment oxidation–reduction reactions, as well as human activities (Li et al. 2012). NH$_4^+$–N was the second dominant N

Fig. 1 Burial fluxes of total nitrogen and total phosphorus in six sediment cores from E1, E2, E3, M, Y1, and Y2 in the different lake area of China showing N concentration versus time
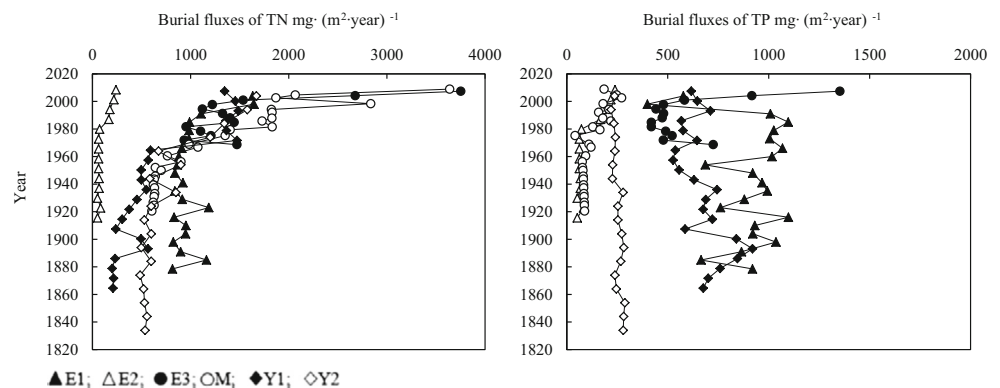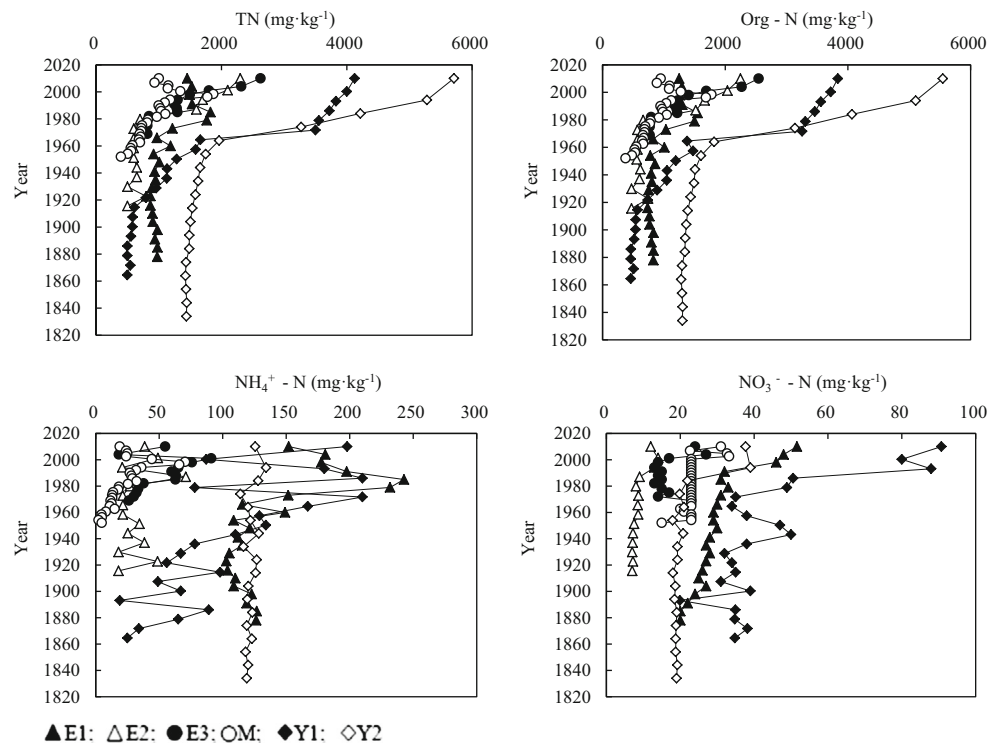
Fig. 2 Content of TN and N forms in six sediment cores from E1, E2, E3, M, Y1, and Y2 in the different lake area of China showing N concentration versus time

▲ E1:   △ E2:   ● E3: ○ M: ◆ Y1:   ◇ Y2

form in the sediment cores and accounted for 2–12 % of TN. The order of NH_4^+–N was E1 > Y2 > Y1 > E3 > E2 > M, with an average of 140, 123, 102, 50, 966, and 24 mg·kg^{-1}, respectively. NH_4^+–N content illustrated no significant regularity but resulted in surface enrichment. This increasing NH_4^+–N on one hand could have been attributable to increasing anthropogenic impacts. On the other hand, this could be resultant from NH_4^+–N carrying a positive electron, making it easily absorbed to colloid surfaces that carry a negative electron. NH_4^+–N in E1 and Y1 generally fluctuated, which reflects the more serious N pollution, the more unstable and volatile NH_4^+–N in sediments.

NO_3^-–N accounted for an average of only 1.7 % of TN in sediment cores. The order of NO_3^-–N was Y1 > E1 > M > Y2 > E3 > E2, with an average of 44, 30, 25, 21, 17, and 9 mg·kg^{-1}, respectively. NO_3^-–N had an increasing trend after the 1980s, which was consistent with TN processes for past decades. Transformations were also associated with characteristics of NO_3^-–N. Specifically, nitrification transforms NH_4^+–N into NO_3^-–N, which is important because of high oxygen levels in surface sediments that lead to NO_3^-–N increases.

The relationship between TN and N forms showed that TN was significantly positively correlated with organic-N ($r=0.871$; $n=232$; $P<0.01$) but was not clearly correlated with NH_4^+–N and NO^{3-}–N.

Temporal distribution of TP and P forms

TP and P contents and forms versus sample age of the six cores are presented in Fig. 3. The TP sequence in sediments

was Y1 > Y2 > E3 > E1 > E2 > M, with means of 1066, 685, 631, 627, 466, and 199 mg·kg^{-1}, respectively. A spatial distribution similar to that of TN was observed, e.g., Yungui Plateau lakes > Eastern Plain lakes > Mountain Mongolia–Xinjiang lakes. Furthermore, the vertical profiles of TP content showed dramatic increases in sediments from different lakes, with average increases reaching 161 % since the 1980s.

P was divided to organic P, Fe/Al–P, and Ca–P. The organic P represents the potential bioactive P in sediments (Baldwind et al. 2001), which is mainly derived from biological residues, humic and fulvic acid associated with OM, agricultural non-point source (NPS) pollution, and domestic sewage (Ruban 2001). OP was the third dominant P form in the sediment cores, which accounted for 14–42 % with an average of 28 %. It showed a similar increasing trend with that of TP, and was significantly positively correlated with TP in the cores ($r=0.965$; $n=232$; $P<0.01$).

The Fe/Al–P, which represents P bound to oxides and hydrates of aluminum, iron, and manganese, was the highest bioactive in the sediments (Reddy et al. 1995). Fe/Al–P is mainly derived from domestic sewage and industrial wastewater (Ruban 2001). The Fe/Al–P content accounted for 15–51 % of TP in the sediment cores with an average proportion of 31 %. Spatial distribution of Fe/Al–P was: Y1 > E1 > E2 > E3 > Y2 > M, with a mean concentration of 384, 276, 229, 215, 97, and 13 mg·kg^{-1}, respectively. This result indicated that along with more domestic and industrial pollution, the higher the level of Fe/Al–P in sediments. Consequently, Fe/Al–P levels could be used as a pollutant indicator for lake

Fig. 3 Fractions of phosphorus in six sediment cores from E1, E2, E3, M, Y1, and Y2 in the different lake area of China showing P concentration versus time

▲ E1: △ E2: ● E3: ○ M: ◆ Y1: ◇ Y2
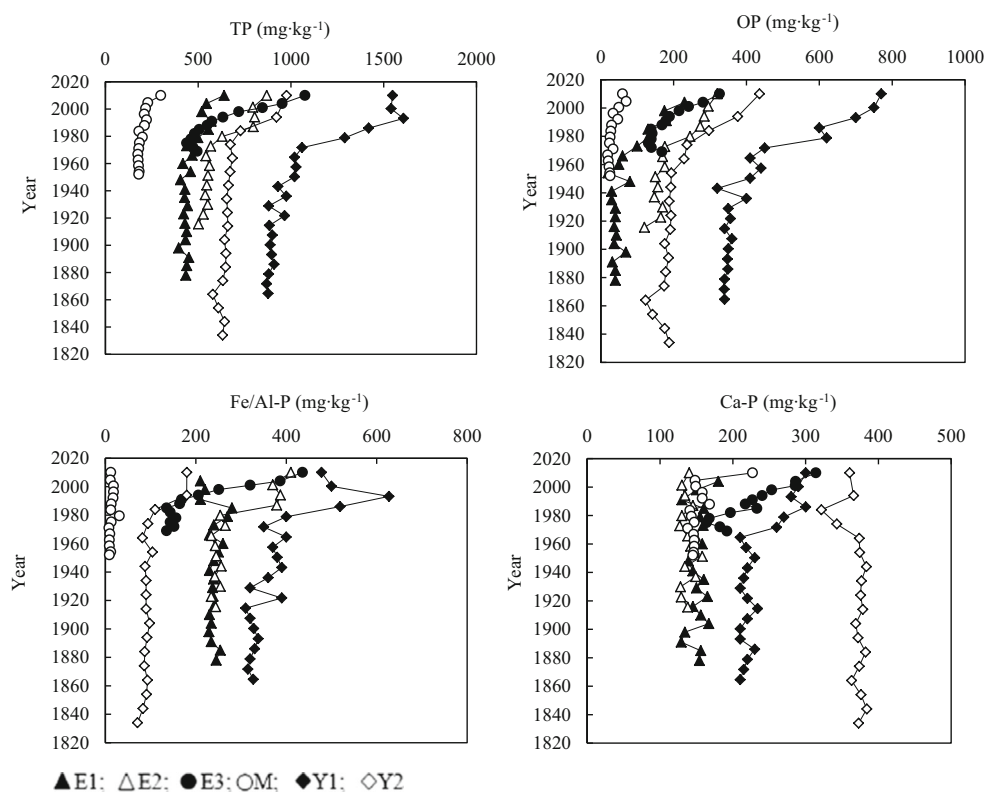
environments. Historical Fe/Al–P had an increasing trend from the 1980s to 2000 in sediments cores. However, a decreasing inflection point appeared in 2000 (excluding that for E3), which may be attributed to heightened regulations for domestic and industrial pollution in these watersheds.

The Ca–P, which represents P bound to calcium, accounted for 22–80 % of TP in sediments, with a relatively high proportion in the M core. Spatial distribution of Ca–P following this sequence: Y2 > Y1 > E3 > M > E1 > E2, with mean values of 369, 236, 215, 154, 151, and 137 mg·kg^{-1}, respectively. This suggests that Ca–P distribution is largely dependent on lake position and naturally occurring background calcium levels in soils within the watershed. Soil in cores Y1, Y2, E3, and M were alkaline, and rich in carbonate apatite, and consequently had high amounts of calcium in lake sediments. In contrast, soil in cores E1 and E2 were acidic, with calcium being easily exchangeable. Historical distribution of Ca–P in cores Y1, E3, and M had an increasing trend since the 1980s whereas other cores scarcely exhibited any change.

Discussion

Relationships between socioeconomic progress and records of sediment BFs

The burial processes of sediment nutrients were significantly influenced by several factors, such as nutrients source,

sedimentary rate, hydrodynamic conditions, bioturbation, and the redox environment (Lu et al. 2005). China has many types of lakes, resulting in very high spatial heterogeneity due to the differences in geologic, geomorphologic, and climatic characteristics. A strong relationship was found by comparing the economic development and the structure of pollutants with records of TN and TP BFs of sediments in the regions under investigation herein. This influence could be divided into three stages.

Before the 1980s, most of the lakes in China were primarily affected by natural processes. Generally, these lakes had adequate water quality with lower nutrient levels because of low exogenous loading. China's economy has intensified dramatically since 1978, with the national GDP reaching as high as US$119.8 billion, nearly thrice as much as the amount at the end of the 1990s. The population also increased by 280 million during the same period. These changes led to the dramatic increase in sewage discharge from 31.5 billion tons to 45 billion tons, which annually increased by approximately 7 %. Accordingly, the nutrients primarily derived from industrial processes, urbanization (i.e., N growth was particularly noticeable; Fig. 4a).

After 2000, the national GDP maintained an average growth of 8 %, with increases to roughly US$7301 billion by the end of 2012. This increase was nearly 244 times greater, with the population increasing to 340 million. Furthermore, annually, total amount of sewage discharge had been growing at 4 %. Considerable changes occurred in the structure of
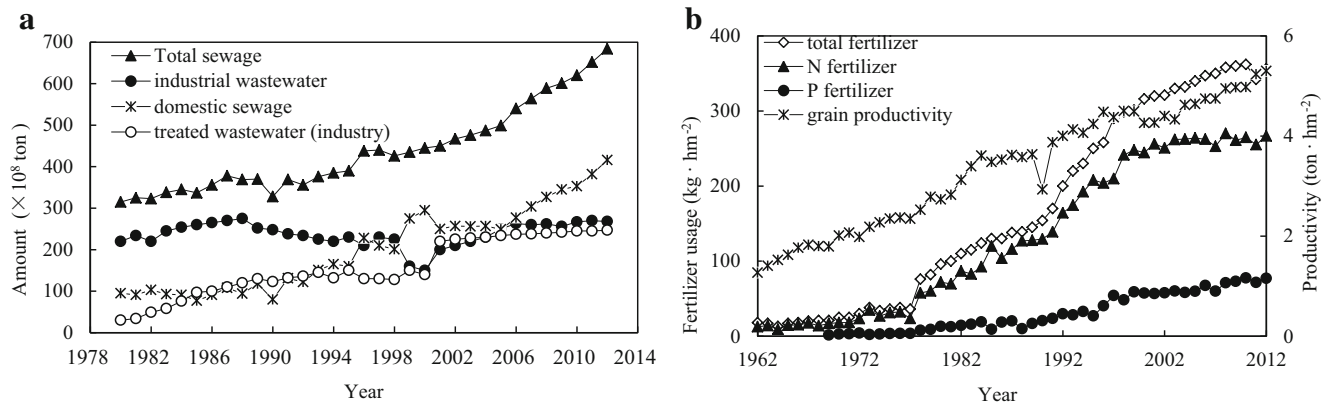
Fig. 4 Historical input amount of sewage (**a**) and usage of artificial N, P fertilizer, and corresponding food productivity in China (**b**)

pollution loading. Since then, agricultural NPS pollution and domestic sewage has become the primary sources of pollutants as a result of rapid urbanization and agricultural intensification. The steady increase in nutrient amount caused rapid deterioration of aquatic ecosystem. Consequently, aquatic habitats gradually transformed from "grass-type lakes" to "algal-type lakes" (Cheng and Li 2006; Ni et al. 2011). Numbers of aquatic plants began decreasing, and thereby depositing plant tissue which resulted in dramatic increases organic matter in sediment (Fig. 5). The increasing organic matter in turn increased the porosity and reduced the bulk density of sediments. These changes ultimately decreased BFs of nutrients, all of which coalesced the acceleration of lake eutrophication and ecological deterioration.

The Chinese State Council and concerned local governments have strengthened the control of exogenous input loadings in key watersheds (i.e., Taihu Lake, Chaohu Lake, Dianchi Lake, and Ulansuhai Lake) to address the series of negative consequences caused by aquatic ecosystem deterioration and to protect the ecological environment and human health (Liu et al. 2014). Targeted activities have included waste water treatment plants (WWTPs), lake peripheral pollution

interception, agricultural non-point sources control, lake ecological restoration and dredging, and the control of inflowing river pollution (Ministry of Environmental Protection of China 2012b; Liu et al. 2014; Zhang et al. 2014). The trend of excessive industrial sewage discharge has been gradually controlled, especially that of industrial pollution. At present, the treatment rate of industrial wastewater has already exceeded 90 % (Wu et al. 2011). Compared the dynamics of nutrient at the sediment from different watersheds, suggested that the increase rate of BFs of nutrient in sediment was slowed down when implementation of pollution control policies, such as E1, E2, M, and Y1. However, when no load reduction in watersheds occurred, the increase rate of nutrient in sediment would continue to increase, as was the case for E3 and Y2.

Y1 (Dianchi Lake) was selected as an example to further study the role of economic progress on nutrient accumulation in the sediment. The basin accounted for only 0.7 % of the area but GDP accounting for 24 % of the Yunnan Province, which resulted in it being the most serious eutrophic lake in China (Yang et al. 2010). Figure 6 presents an overview of the economy, aquatic ecosystem, water quality, and nutrients BFs in sediment cores from Dianchi Lake during the past 60 years. The basin had a population of about 3.78 million and GDP about US$0.27 billion before 1980, with the agricultural population accounting for nearly 70 %. From 1980 to 2000, the population increased by 27 %, whereas the proportion of agricultural population dramatically decreased and accounted for only 50 % of the total population, and the GDP increased six times, which leads to nutrient loading on the lakes. Accordingly, the concentration of TN and TP in water increased eight and five times, and the water quality was grade as class III to V according to the water environment quality standard for surface water (GB3838-2002) in China. After 2000, the economy level and the population grew faster than before, this situation lead to the overall deterioration of the aquatic ecosystem, with 24 species of aquatic plants and 95 species of phytoplankton disappearing, whereas the density of algae increased dramatically, remained steady at $1.3 \times 10^{8} \cdot a \cdot L^{-1}$.
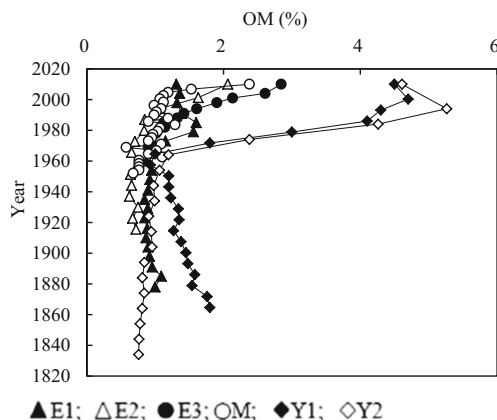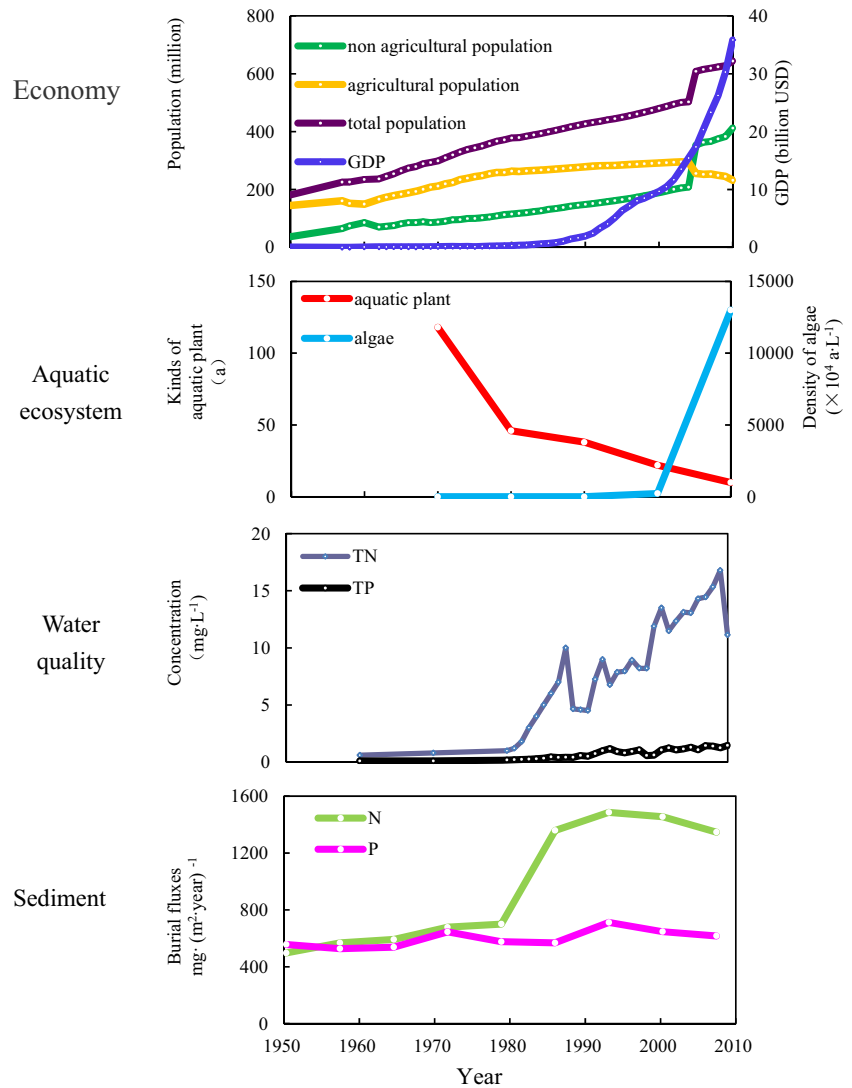

Fig. 5 Content of organic matter in dated sediment samples from the different lakes

Fig. 6 Temporal variation of economy, aquatic ecosystem, and water quality as well as sediment NP burial fluxes in Dianchi Lake

In this study, the increased rate of BFs of TN in the sediment cores was considerably higher than that of TP, which was partly related to the long-term fertilization practices of Chinese farmers. Agriculture in China is with a limited area with large inputs of artificial fertilizers and other resources (Guo et al. 2010). The excessive use of synthetic N and P fertilizers resulted in serious environmental problems. However, farmers still preferred N and P fertilizers, with the application dosage of N fertilizers being significantly higher than that of P fertilizers (Ju et al. 2009). Fig. 4b presents an overview of fertilizer use and the main crop productivity in China during the past 50 years. Agriculture in China has greatly intensified since the early 1980s. N and P fertilizer applications and grain production in 2012 reached 33.1 million, 9.2 million, and 590 million tons, respectively. These values represented increases of 390, 320, and 180 % compared with those in 1980. At present, the application of N fertilizer is

three times greater than of P fertilizers, and the leaching rate of N from soil to the environment is also much higher than that of P (Xie et al. 2013). Eventually, dosage and nutrient liability became key factors in why more N has accumulated in lake sediments during past decades.

Relationships between basin development and records of sediment N and P forms

The content variations of TN and TP levels and their forms among the different lakes are mainly affected by the lake position and anthropogenic activities in the watersheds (Tiyapongpattana et al. 2004, Ishii et al. 2010). Cores Y1 and Y2 are located at nearly the same position, and the GDP, population density, and exogenous nutrients load from core Y1 were much higher than those from core Y2. However, the content of nutrients in sediments from Y1 was much lower

than those from Y2. Similar phenomenon was also found in the sediments from the rest of the lakes in this study (Table 1). The results indicated that conservation implementation should not only concentrate in economically developed areas, but also in the economically backward areas with high risks of potential nutrients release from sediments. Generally, the content of nutrients in sediment from different lake area were in the order of Yungui Plateau lakes > Eastern Plain lakes > Mongolia–Xinjiang lakes. This is largely attributed to the multiple effects of water depth, hydrodynamic, and nutrients background and climate, and economic status. Most of the lakes in Yungui Plateau have deep water levels. Accordingly, sedimentary nutrients were less affected by the wind and water movement, resulting in more nutrients easier to bury in the sediment rather than release. In contrast, most of the lakes in Eastern Plain are shallow lakes (water depth generally less than 6 m), and the sediments are strongly disturbed by water hydrodynamics and erosion compared with Yungui Plateau lakes, resulting in sediment re-suspension occurring frequently (Wu and Hua 2014). Finally, the contents of nutrients in the lakes were considerably lower than those in Yungui Plateau lakes even though most of these lakes had higher pressure per unit volume of nutrients loadings. Most of the lakes in Mountain Mongolia–Xinjiang are cover an area with an undeveloped economy (Zhang et al. 2011), with nutrient levels typically remaining low.

The nutrient fractions also displayed variability among lakes. Organic-N and OP in the sediment cores have steadily increased since the early 1980s. This increase mirrored the rapid development of agricultural intensification and urbanization in China in the early 1980s, which increased the number of organic pollutants on the lakes. The Fe/Al–P form exhibited an ascending trend during this period in cores E1, E3, and Y1. This trend is consistent with the development of economy due to these basins are the major processing and manufacturing areas in China. Ca–P presented an obvious increasing trend in cores E3 and M since the 1980s, which was consistent with the gradual intensification of soil loss in North China caused by the destruction of vegetation.

After 2000, the amounts of organic-N and OP in all sediment cores had greatly increased, which has reflected increasing pollution derived from agricultural and domestic pollution. In addition, the increase of Org-N and OP was also attributed to the contemporary sedimentation of organic-bound P as phytoplankton or macrophytes and its accumulation in the upper sediment layer (Zhang et al. 2008). Fe/Al–P and Ca–P decreased in some lakes due to implementation of a series of environmental protection projects to control soil erosion and industrial pollution in key watersheds during the mid-1990s.

N and P nutrient structure and its indicative significance

The structure of the aquatic biological community of the lakes was strongly affected by the amounts of N and P, as well as the interaction between N and P (He and Han 2010). The mean value of N/P in water from different lakes for this study was 19, which indicated that P was the dominant limiting factor for algal growth in lakes in China according to the nutrient limitation characteristic of the eutrophication assessment standard (Guildford and Heeky 2000). Results herein were consistent with that of Cai et al. (2010), who analyzed numbers of N/P in water from different lakes in China.

Lake N/P levels of water throughout China have increased since 2000 (Fig. 7), before which N/P was slightly static with a mean value of 16. Thereafter, it gradually increased, with the mean value reaching 22. This was partly attributed to the implement of policies of "P loading reduction" in the late 1990s, which largely reduced the P loading in the lakes (Zhang et al. 2014). The mean value of the N/P of input loading and sediments was 13 and 2.8, respectively (Fig. 7), which was much less than the N/P ratio of the water. This could be associated with the gradually growth of phytoplankton in water and the release difference of N and P from sediment.

To further study the historical role of phytoplankton N fixation on N/P in water, Qian et al. (1997) established a method to evaluate the contribution of aquatic organic-N and terrestrial organic-N on marine system by utilizing the C/N ratio.
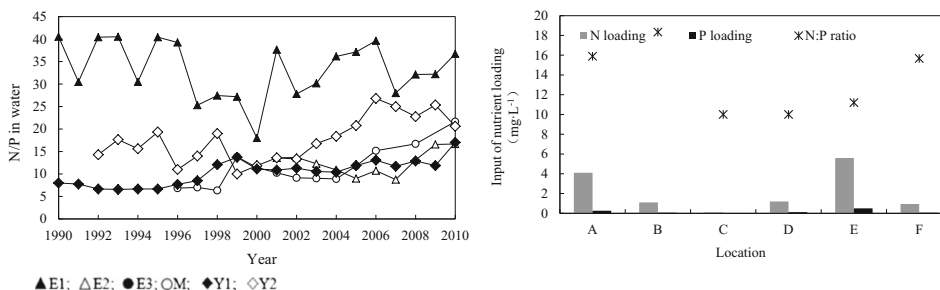
Fig. 7 N/P of water, sediments and external input loading in different lakes

Assuming that the C/N ratios of aquatic and terrigenous OM were 5 and 20, respectively, the following formula was obtained:

Na=(20TN−TOC)/15, (Na representing the content of aquatic organic-N)

Nt= (TOC− 5TN)/15, (Nt representing the content of terrestrial organic-N)

Figure 8 presents the historical ratio of aquatic organic-N for TN in sediments from different lakes. Aquatic organic-N bound sediment presented an increasing trend, which accompanied the "algae-type" phenomenon developed rapidly in most of China's lake since 2000. These additions represent massive reservoirs of N that will continuously increase long even after exogenous N loading is controlled.

The difference release between N and P is another important factor which leads to N/P gradually increasing. Burial efficiency could be used as a tool to assess the potential release of N and P from sediment, which was calculated by using the following formula (Ingall and Jahnke 1994),BE=BF/(BF+W)×100 %).

Where BE is burial efficiency, %; BF is the BFs of the biogenic elements, mg·(year·m^2)$^{-1}$; and W is the diffusion flux, mg·(year·m^2)$^{-1}$. The BE of TN and TP in the surface sediment in selected lakes are shown in Fig. 9. The BE of P in sediments was higher than that of N, >suggesting that sediment N was more easily released to water compared to P.

Protection recommendations for Chinese lakes

Actions to control eutrophication of lakes in China have been adopted for nearly 30 years. These actions have passed through the development, utilization, and management stage (1980s); the protection and integration governance stage (1990s); and the planning and control

stage (since 2005) (Xu et al. 2011). However, the trend of lake eutrophication in China still has not significantly reduced despite issuing a series of engineering and management measures. Table 2 gives the current management strategies and underlying disadvantage. The main disadvantage have included simple treatment methods, low-intensity investment in pollution control, institutional fragmentation (vertically and horizontally), and lack of meaningful endogenous pollution control strategies.

According to the relationship between historical BFs, forms of nutrients in sediment and N/P in water as well as Chinese economic development and population expansion, suggested that socioeconomic progress of China is growing largely at the expense of the quality of its aquatic ecology and environments. Therefore, nutrients export resulting from economic development should be taken into account during the formation of basin management strategies for the lake water environment. The following targeted activities are recommended in this study: (i) the industrial structure should be further adjusted, and economic development model should be converted from extensive to intensive economic procedures as to effectively reduce nutrient loading; (ii) regarding pollution source control terms, not only should industrial pollution be regulated, but also addressed to promote the governance of domestic pollution and agricultural NPS pollution. Scientific and effective agricultural NPS pollution control technologies should be given priority to development. And finally, (iii) ecological protection should be given additional attention. Conducting lake ecological restoration plans should be continued to control algal growth and restore aquatic biota while maintaining environmental condition and reducing the release of nutrients from sediment; and, (iv) current lake protection should not only be limited to Eastern Plain lakes and seriously polluted lakes but also to other regions with currently high water quality.
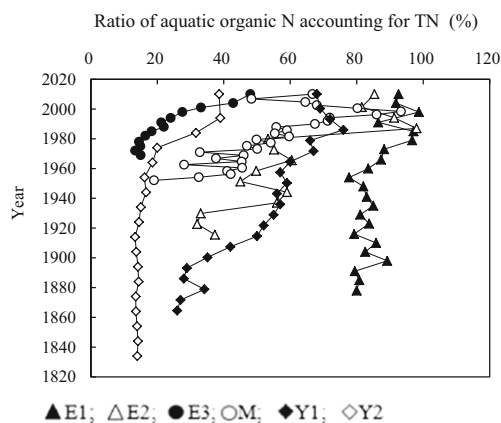

Fig. 8 Historical percentage of aquatic organic N accounts for TN in different sediment cores
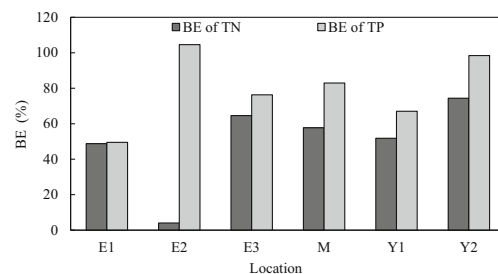

Fig. 9 BE of TN and TP in surface sediments from different lakes. Data of TN was calculated from: E1– Zhang et al. (2006); E2 – Pan et al. (2007); E3 – Cai et al. (2007); M – Sun et al. (2006); Y1–Unpublished data; Y2 – Ni and Wang (2015). Data of TP was calculated from: E1– Fan et al. (2006); E2 –Zhang et al. (2008); E3 –Cai et al. (2007); M – Guan et al. (2013); Y1–Unpublished data; Y2 – Ni and Wang (2015)

Table 2　Main disadvantage of lake management in current strategy of China

Item	Disadvantage	Measure
	Ignoring protection	Emphasis on pollution governance
Region	Ignoring other regional lakes	Mainly concentrated in the Eastern Plain lakes
Object	Ignoring protection of lakes that have good water quality status	Mainly concentrated in the serious polluted lakes
Scope	Ignoring the protection of watershed	Just emphasis on lake itself
Technology roadmap 1	Ignoring the protection of aquatic ecosystem	Emphasis the protection of water quality
Technology roadmap 2	Ignoring ecological restoration	Emphasis the control of pollution source
Pollution source control	Ignoring the control of agricultural NPS pollution and domestic pollution	Emphasis the control of industrial pollution

Conclusion

This study reconstructed the historical accumulation of nutrients and the relationship between basin economic progresses on nutrient accumulation in sediments of Chinese lakes. Results suggested that the BFs of TN increased in sediment cores, whereas TP levels were consistent or only slightly increased, except in highly polluted lakes during the past decades. Similar process was also found in the concentration of nutrients in water (i.e., increased N/P). This historical distribution pattern was mainly controlled by the long-term fertilization practices of farmers in the watershed (N fertilization exceeds that of P) and was contingent upon pollution control policies (e.g., emphasized P whereas N was ignored).

Vertical profiles of BFs indicated that the lake nutrients accumulation history mainly included three stages in China. Nutrient accumulation started in the 1980s, accelerated from the 1990s, and declined after 2000. Before the 1980s, nutrients were relatively low and stable and mainly controlled by natural processes. Thereafter, N in whole sediments and P in seriously polluted sediments dramatically increased due to the increasing influence of anthropogenic processes. Nutrients were primarily derived from industries and domestic sewage. After 2000, BFs of nutrients were gradually steady and even had a decreasing trend because of the implementation of watershed load reduction policies. The decreasing NaOH-extracted P (Fe/Al–P) and increasing organic P indicated that the source of exogenous pollution was undergoing a shift. Inputs of nutrients were dominant from agricultural and domestic sewage, whereas industrial pollution has been gradually controlled in most watersheds. Historical nutrient dynamics implies that the economy of China is growing at the expense of the quality of its aquatic ecological environment.

Relationship between historical BFs, forms of nutrients in sediment and N/P in water, as well as Chinese economic development and population expansion, suggests that socioeconomic progress of China is growing largely at the expense of the quality of aquatic ecology and environments. The following targeted activities are recommended in this study: promoting transformation of the basin economic and social development model; constructing an effective lake pollution control technology system; synchronizing the protection of polluted lakes and those with good water quality, and, strengthening aquatic ecological restoration and protection.

References

Baldwind S, Beattie JK, Coleman LM (2001) Hydrolysis of an organophosphate ester by manganese dioxide. Environ Sci Technol 35(4):713–716

Cai JB, Li WQ, Liu N, Pang Y (2007) Characteristics of contaminated sediments in Yanghe Reservoir. J Agro-Environ Sci 26(3):886–893 **(in Chinese)**

Cai LY, Li Y, Zheng ZH (2010) Temporal and spatial distribution of nitrogen and phosphorus of lake systems in China and their impact on eutrophication. Earth Environ 38(2):235–241

Carpenter SR (2005) Eutrophication of aquatic ecosystems: bistability and soil phosphorus. Proc Natl Acad Sci U S A 102:10002–10005

Chen X, Yang XD, Dong XH, Liu EF (2013) Environmental changes in Chaohu Lake (southeast, China) since the mid 20th century: the interactive impacts of nutrients, hydrology and climate. Limnologica 43:10–17

Cheng XY, Li SJ (2006) Eutrophication evolution and their characteristics of the typical lakes of Yangtze River. Chin Sci Bull 51(7):848–855

Conley DJ, Paerl HW, Howarth RW, Boesch DF, Seitzinger SP, Havens KE (2009) Controlling eutrophication: nitrogen and phosphorus. Science 323:1014–1015

Fabricius KE (2005) Effects of terrestrial runoff on the ecology of corals and coral reefs: review and synthesis. Mar Pollut Bull 50(2): 125–146

Fan CX, Zhang L, Bao X, You B, Zhong J, Wang J, Ding SM (2006) Mobile mechanism of biogenic elements and their quantification on the sediment-water interface of Lake Taihu: II. Chemical thermodynamic mechanism of phosphorus release and its source-sink transition. J Lake Sci 18(3):207–217 (in Chinese)

Guan R, Lu CW, He J, Wang JH, Hou DK, Xie ZL (2013) Diffusion fluxes of phosphorus across water–sediment interface in Lake Wuliangsuhai and Daihai. J Agro-Environ Sci 32(8):1609–1617 (in Chinese)

Guildford SJ, Heeky RE (2000) Total nitrogen, total phosphorus, and nutrient limitation in lakes and oceans: is there a common relationship. Limnol Oceanogr 45(6):1213–1223

Guo JH, Liu XJ, Zhang Y, Shen JL, Han WX, Zhang WF, Christie P, Guolding KWT, Vitousek PM, Zhang FS (2010) Significant acidification in major Chinese croplands. Science 327:1008–1010

He JS, Han XG (2010) Ecological stoichiometry: searching for unifying principles from individuals to ecosystems. Chin J Plant Ecol 34(1): 2–6

Ingall E, Jahnke R (1994) Evidence for enhanced phosphorus regeneration from marine sediments overlain by oxygen depleted waters. Geochim Cosmochim Acta 58(11):2571–2575

Ishii Y, Harigae S, Tanimoto S, Yabe T, Yoshida T, Taki K, Tatsumoto H (2010) Spatial variation of phosphorus fractions in bottom sediments and the potential contributions to eutrophication in shallow lakes. Limnol 11(1):5–16

Jin XC, Liu HL, Tu QY (1990) Chinese lake eutrophication. Chinese Research Press of Environmental Science, Beijing

Jones DL, Willett VB (2006) Experimental evaluation of methods to quantify dissolved organic nitrogen (DON) and dissolved organic carbon (DOC) in soil. Soil Biol Biochem 38:991–999

Ju XT, Guang XX, Chen XP, Zhang SL, Zhang LJ, Liu XJ, Cui ZL, Yin B, Christie P, Zhu ZL, Zhang FS (2009) Reducing environmental risk by improving N management in intensive Chinese agricultural systems. Proc Natl Acad Sci U S A 106(9):3041–3046

Li QQ, Huo SL, Jiu FY, Liu QX, Xi BD (2010) The distribution of nutrients and particle size, their correlations in surface sediments of different lakes, China. J Agro-Environ Sci 29(12):2390–2397

Li RZ, Li F, Zhou AJ, Tong F, Qian JZ (2012) Distribution and bioavailability of nitrogen and phosphorus species in the sediments from shiwuli stream in Lake Chaohu. Environ Sci Technol 33(5):1503–1010 (in Chinese)

Liu EF, Shen J, Zhang EL, Wu YH, Yang LY (2010) A geochemical record of recent anthropogenic nutrient loading and enhanced productivity in Lake Nansihu, China. J Paleolimnol 44(1):15–24

Liu Y, Wang YL, Sheng H, Dong FF, Zou R (2014) Quantitative evaluation of lake eutrophication responses under alternative water diversion scenarios: a water quality modeling based statistical analysis approach. Sci Total Environ 468:219–227

Lu XX, Song JM, Yuan HM (2005) Distribution characteristics of nitrogen in the Southern Yellow Sea surface sediments and nitrogen functions in biogeochemical cycling. Geogr Rev 51(2):212–218 (in Chinese)

Ministry of Environmental Protection of China (2012a) Report on the state of the environment in China 2011. http://jcs.mep.gov.cn/hjzl/zkgb/, 2011. [accessed on Aug 24, 2012]

Ministry of Environmental Protection of China (MEP) (2012b) Water pollution control plans for some key basins (2001–2015). http://www.mep.gov.cn/gkml/hbb/bwj/201206/t20120601_230802.htm, 2012.

Nanjing Institute of Soil, Chinese Academy of Science (1978) Soil and physical chemistry analysis. Shanghai Technology Press, Shanghai, pp 121–134 (in Chinese)

Ni ZK (2011) Studies on the history pollution and the sources of organic matter and nitrogen in sediments of Lake. Inner Mongolia Agricultural University press, Inner Mongolia

Ni ZK, Wang SR (2015) Historical accumulation and environmental risk of nitrogen and phosphorus in sediments of Erhai Lake, Southwest China. Ecol Eng 79:42–53

Ni ZK, Wang SR, Jin XC, Jiao LX (2011) Study on the evolution and characteristics of eutrophication in the typical lakes on Yunnan-Guizhou Plateau. Acta Sci Circumst 31(12):2681–2689 (in Chinese)

Ni ZK, Wang SR, Zhang L, Wu ZQ (2015) Historical accumulation of N and P and sources of organic matter and N in sediment in an agricultural reservoir in Northern China. Environ Sci Pollut Res 22(13): 9951–64. doi:10.1007/s11356-015-4169-4

Nyenje PM, Foppen JW, Uhlenbrook S (2010) Eutrophication and nutrient release in urban areas of sub-Saharan Africa—A review. Sci Total Environ 408:447–455

Pan CR, Wang JQ, Zheng ZX, Liu JJ (2007) Forms of phosphorus and nitrogen existing in sediments in Chaohu Lake. J Ecol Rural Environ 23(1):43–47 (in Chinese)

Qian JL, Wang SM, Xue B (1997) A method of quantitative estimate terrigenous organic carbon in lakes research. Sci Bull 42(15): 1655–1657 (in Chinese)

Reddy KR, Diaz OA, Scinto LJ, Agami M (1995) Phosphorus dynamics in selected wetlands and streams of the Lake Okeechobee Basin. Ecol Eng 5(2–3):183–207

Ruban V (2001) Harmonized protocol and reference material for the determination of extractable contents of phosphorus in freshwater sediments—a synthesis of recent works. Fresenius J Anal Chem 370:224–228

Ruban V, López-Sánchez JF, Pardo P (1999) Selection and evaluation of sequential extraction procedures for the determination of phosphorus forms in lake sediment. J Environ Monit 1(1):51–56

Schenau SJ, Reichart GJ, De Lange GJ (2005) Phosphorus burial as a function of paleoproductivity and redox conditions in Arabrian Sea sediments. Geochim Cosmochim Acta 69(4): 919–931

Sun HM, He J, Lu CW, Gao XD, Fan QY, Xue HX (2006) Nitrogen pollution and spatial distribution pattern of Wuliangsuhai Lake. Geogr Res 25(6):1003–1012 (in Chinese)

Tiyapongpattana W, Pongsakul P, Shiowatana J (2004) Sequential extraction of phosphorus in soil and sediment using a continuous-flow system. Talanta 62(4):765–771

Wang SR (2015) Environmental evolution and protection management of Chinese Lakes. Science Press, Beijing

Wu D, Hua ZL (2014) The effect of vegetation on sediment resuspension and phosphorusrelease under hydrodynamic disturbance in shallow lakes. Ecol Eng 69:55–62

Wu YQ, Lu ZJ, An B (2011) The dynamic study on total volume of wastewater discharge in China during 1985-2008. SCI-Tech Inf Dev Econ 21(17):183–185 (in Chinese)

Xie ZY, Zhuo MN, Li DQ, Liao YS, Wei GL (2013) Characteristics of nitrogen and phosphorus loss by runoff from vegetable fields under different fertilization levels. Ecol Environ Sci 22(8):1423–1427 (in Chinese)

Xu QG, Cao JL, Gao RT, Ding JT, Jiang L, Zhang H, Jiang TT (2011) Trend of water quality deterioration and eutrophication control phases partition in China. Environ Sci Technol 34(11):147–151 (in Chinese)

Yang GS, Ma RH, Zhang L, Jiang JH, Yao SC, Zhang M, Zeng HA (2010) Lake status, major problem s and protection strategy in China. J Lake Sci 22(6):799–810 (in Chinese)

Yao SC, Li SJ (2004) Sedimentary records of eutrophication for the last 100 years in Caohu Lake. Acta Sedimentol Sin 22(20):0343–0348 (in Chinese)

Zhang H, Shan BQ (2008) Historical distribution and partitioning of phosphorus in sediments in an agricultural watershed in the Yangtze-Huaihe region. Chin Environ Sci Technol 42: 2328–2333

Zhang JG (2013) Deposition rat, grain- size change characteristics and their environment evolution of sediment cores in Wu- liangsu Lake. Inner Mongolia University press, Inner Mongolia

Zhang L, Fan CX, Wang JJ, Chen YW, Jiang JH (2008) Nitrogen and phosphorus forms and release risks of lake sediments from the middle and lower reaches of the Yangtze River. J Lake Sci 20(3):263–270 (in Chinese)

Zhang L, Fan CX, Wang JJ, Zheng HC (2006) Space–time dependent variances of ammonia and phosphorus flux on sediment-water interface in Lake Taihu. Environ Sci Technol 27(8):539–543 (in Chinese)

Zhang SR, Xu CH, Zhong ZZ, Ren TS, Jing Y (1993) Using ^{210}Pb and ^{137}CS method determination age and deposition rate of sediment in Erhai Lake. Radiat Prot 13(6):453–465 (in Chinese)

Zhang T, Zeng WH, Wang SR, Ni ZK (2014) Temporal and spatial changes of water quality and management strategies of Dianchi Lake in southwest China. Hydrol Earth Syst Sci 18:1–10

Zhang Y, Deng XH, Chen J (2005) Evaluating phosphorus load in sediment of Dianchi Lake. China Environ Sci 25(3):329–333 (in Chinese)

Zhang YL, Xu QJ, Xi BD, Zhang LY (2011) Major problems and control measures of water ecological environment in Inner Mongolia-Xinjiang Plateau. J Lake Sci 23(6):828–836 (in Chinese)