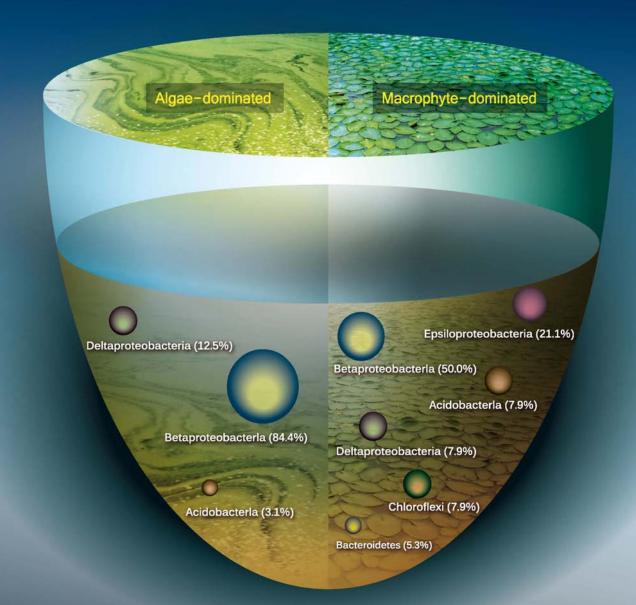


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## CONTENTS

The 5th International Symposium on Environmental Economy and Technology (ISEET-2012)
Sensitive voltammetric and amperometric responses of respiratory toxins at hemin-adsorbed carbon-felt
Yasushi Hasebe, Yue Wang······1055
Destruction of 4-phenolsulfonic acid in water by anodic contact glow discharge electrolysis
Haiming Yang, Baigang An, Shaoyan Wang, Lixiang Li, Wenjie Jin, Lihua Li1063
Nitrous oxide emissions from black soils with different pH
Lianfeng Wang, Huachao Du, Zuoqiang Han, Xilin Zhang ······1071
Coulometric determination of dissolved hydrogen with a multielectrolytic modified carbon felt electrode-based sensor
Hiroaki Matsuura, Yosuke Yamawaki, Kosuke Sasaki, Shunichi Uchiyama
Palladium-phosphinous acid complexes catalyzed Suzuki cross-coupling reaction of heteroaryl bromides
with phenylboronic acid in water/alcoholic solvents
Ben Li, Cuiping Wang, Guang Chen, Zhiqiang Zhang
Aquatic environment
Organic matter produced by algae and cyanobacteria: Quantitative and qualitative characterization
Maud Leloup, Rudy Nicolau, Virginie Pallier, Claude Yéprémian, Geneviève Feuillade-Cathalifaud
Effects of environmental factors on sulfamethoxazole photodegradation under simulated sunlight irradiation:
Kinetics and mechanism
Junfeng Niu, Lilan Zhang, Yang Li, Jinbo Zhao, Sidan Lv, Keqing Xiao
Irrigation system and land use effect on surface water quality in river, at lake Dianchi, Yunnan, China
Takashi Tanaka, Takahiro Sato, Kazuo Watanabe, Ying Wang, Dan Yang, Hiromo Inoue, Kunzhi Li, Tatsuya Inamura1107
Temporal and spatial changes in nutrients and chlorophyll-a in a shallow lake, Lake Chaohu, China:
An 11-year investigation
Libiao Yang, Kun Lei, Wei Meng, Guo Fu, Weijin Yan ·····1117
Phosphorus speciation in the sediment profile of Lake Erhai, southwestern China: Fractionation and <sup>31</sup> P NMR
Runyu Zhang, Liying Wang, Fengchang Wu, Baoan Song ·····1124
Effect of ammonium on nitrous oxide emission during denitrification with different electron donors
Guangxue Wu, Xiaofeng Zhai, Chengai Jiang, Yuntao Guan
Adsorption of 2-mercaptobenzothiazole from aqueous solution by organo-bentonite
Ping Jing, Meifang Hou, Ping Zhao, Xiaoyan Tang, Hongfu Wan1139
Differences in rheological and fractal properties of conditioned and raw sewage sludge
Hui Jin, Yili Wang, Ting Li, Yujing Dong, Junqing Li
Competitive sorption between $17\alpha$ -ethinyl estradiol and bisphenol A/ 4-n-nonylphenol by soils
Jianzhong Li, Lu Jiang, Xi Xiang, Shuang Xu, Rou Wen, Xiang Liu
Determination of estrogens and estrogenic activities in water from three rivers in Tianjin, China
Kaifeng Rao, Bingli Lei, Na Li, Mei Ma, Zijian Wang

#### **Terrestrial environment**

Adsorption and desorption characteristics of diphenylarsenicals in two contrasting soils	
Anan Wang, Shixin Li, Ying Teng, Wuxin Liu, Longhua Wu, Haibo Zhang, Yujuan Huang, Yongming Luo, Peter Christie …1172	
Evaluation of remediation process with soapberry derived saponin for removal of heavy metals from	
contaminated soils in Hai-Pu, Taiwan	
Jyoti Prakash Maity, Yuh Ming Huang, Cheng-Wei Fan, Chien-Cheng Chen, Chun-Yi Li,	
Chun-Mei Hsu, Young-Fo Chang, Ching-I Wu, Chen-Yen Chen, Jiin-Shuh Jean	
contaminated soils in Hai-Pu, Taiwan Jyoti Prakash Maity, Yuh Ming Huang, Cheng-Wei Fan, Chien-Cheng Chen, Chun-Yi Li, Chun-Mei Hsu, Young-Fo Chang, Ching-I Wu, Chen-Yen Chen, Jiin-Shuh Jean	

### Environmental biology

Vertical diversity of sediment bacterial communities in two different trophic states of the eutrophic
Lake Taihu, China (Cover story)
Keqiang Shao, Guang Gao, Yongping Wang, Xiangming Tang, Boqiang Qin1186
Abundance and diversity of ammonia-oxidizing archaea in response to various habitats
in Pearl River Delta of China, a subtropical maritime zone
Zhixin Li, Wenbiao Jin, Zhaoyun Liang, Yangyang Yue, Junhong Lv
Environmental catalysis and materials
Effect of pretreatment on Pd/Al <sub>2</sub> O <sub>3</sub> catalyst for catalytic oxidation of o-xylene at low temperature
Shaoyong Huang, Changbin Zhang, Hong He
Efficient visible light photo-Fenton-like degradation of organic pollutants using in situ surface-modified
BiFeO <sub>3</sub> as a catalyst
Junjian An, Lihua Zhu, Yingying Zhang, Heqing Tang1213
Basic properties of sintering dust from iron and steel plant and potassium recovery
Guang Zhan, Zhancheng Guo ······1226
Degradation of direct azo dye by Cucurbita pepo free and immobilized peroxidase
Nabila Boucherit, Mahmoud Abouseoud, Lydia Adour
Environmental analytical methods
Determination of paraquat in water samples using a sensitive fluorescent probe titration method
Feihu Yao, Hailong Liu, Guangquan Wang, Liming Du, Xiaofen Yin, Yunlong Fu1245
Chemically modified silica gel with 1-f4-[(2-hydroxy-benzylidene)amino]phenylgethanone:
Synthesis, characterization and application as an efficient and reusable solid phase extractant
for selective removal of Zn(II) from mycorrhizal treated fly-ash samples
R. K. Sharma, Aditi Puri, Anil Kumar, Alok Adholeya

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## Temporal and spatial changes in nutrients and chlorophyll-*a* in a shallow lake, Lake Chaohu, China: An 11-year investigation

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#### Abstract

Temporal and spatial changes of total nitrogen (TN), total phosphorus (TP) and chlorophyll-*a* (Chl-*a*) in a shallow lake, Lake Chaohu, China, were investigated using monthly monitoring data from 2001 through 2011. The results showed that the annual mean concentration ranges of TN, TP, and Chl-*a* were 0.08–14.60 mg/L, 0.02–1.08 mg/L, and 0.10–465.90 µg/L, respectively. Our data showed that Lake Chaohu was highly eutrophic and that water quality showed no substantial improvement during 2001 through 2011. The mean concentrations of TP, TN and Chl-*a* in the western lake were significantly higher than in the eastern lake, which indicates a spatial distribution of the three water parameters. The annual mean ratio of TN:TP by weight ranged from 10 to 20, indicating that phosphorus was the limiting nutrient in this lake. A similar seasonality variation for TP and Chl-*a* was observed. Riverine TP and NH<sub>4</sub><sup>+</sup> loading from eight major tributaries were in the range of  $1.56 \times 10^4$ – $5.47 \times 10^4$  and  $0.19 \times 10^4$ – $0.51 \times 10^4$  tons/yr over 2002–2011, respectively, and exceeded the water environmental capability of the two nutrients in the lake by a factor of 3–6. Thus reduction of nutrient loading in the sub-watershed and tributaries would be essential for the restoration of Lake Chaohu.

**Key words**: eutrophication; Lake Chaohu; nitrogen; phosphorus **DOI**: 10.1016/S1001-0742(12)60171-5

#### Introduction

Surface water eutrophication has become a widespread problem with the intensification of human activities (Yan et al., 2010; Carpenter et al., 1998; Smith et al., 1999). Nitrogen and phosphorus enrichment from agriculture, industrial waste and sewage has been correlated with the increased eutrophication of lakes in the past decades (Padisák et al., 2007). Shallow lakes are important in servicing humankind with nutrition, water for drinking, and irrigation (Schinaler, 1977). Due to their proximity to population centers and sensitivity to land use changes eutrophication is one of the main environmental problems in many shallow lakes worldwide (Moss et al., 2005; van Puijenbroek et al., 2004). Current trends in lake eutrophication suggest that nitrogen and phosphorus levels are still increasing due to their excessive loading in terrestrial ecosystems

Similar to many developing countries, water pollution is one of the most critical environmental problems in China. It was reported that more than 90% of the Chinese lakes

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were eutrophic due to excessive nitrogen and phosphorus loading, which has brought high risk to human health (Liu et al., 2003). Lake Chaohu is a shallow lake in China, and once played a significant role in supporting local development. However, this lake is well-known for its anthropogenic eutrophication and microcystin algal blooms (Yang et al., 2011). Lake Chaohu together with other two eutrophic lakes, Taihu and Dianchi often serve as good examples for studying anthropogenic impacts on aquatic ecosystems in China. In order to improve the water quality and control eutrophication in Lake Chaohu, some recovery strategies have been carried out during recent years. Unfortunately, this lake has remained highly eutrophic with loss of ecological function and services, which brought serious threats to drinking water security for more than one million people (Sun and Liu, 1991). Thus we expect that research, monitoring, and evaluation activities are essential for establishing effective measures for addressing the eutrophication of this lake. To the best of our knowledge, many studies have reported the nutri-· Jeso · Jo · Ol ent distribution in water and sediments profiles in Lake Chaohu (Pan et al., 2007); however, the long-term trends

and changes in water quality of this lake have remained unknown, and the export of nutrients from tributaries to this lake has rarely been studied.

Here an 11-year observation was conducted from 2001 through 2011. The monthly concentration of nitrogen phosphorus, and phytoplankton Chl-*a* in Lake Chaohu and in eight major tributaries was investigated. Through this study two questions were expected to be well understood: (1) What are the temporal and spatial changes of water quality in Lake Chaohu? (2) What is the role of riverine nutrients exports for lake eutrophication?

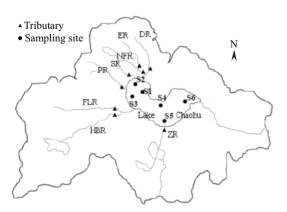
#### 1 Materials and methods

#### 1.1 Sites description

Lake Chaohu (117.00°E–118.29°E, 30.56°N–32.02°N) is located in the Anhui Province of Southeast China, with an average depth of 2.7 m and a surface water area of 573 km<sup>2</sup> (**Fig. 1**). This lake is the fourth-largest freshwater lake of China with a relatively long stagnation time. During recent decades, Lake Chaohu has suffered from serious pollution resulting from substantial discharge of urban wastewater and agricultural runoff. Consequently, the water quality has degraded dramatically and algae blooms occurred frequently.

There are thirty three tributaries entering Lake Chaohu. The Nanfei, Hangbu, Fengle, Shiwuli, Pai, Dianbu, Ershibu, and Zhao Rivers are the major tributaries that contribute most of the total water discharge into the lake (about 90%). With the local-regional development, these rivers have been seriously contaminated by agricultural runoff and industrial wastewater. In this study, one sampling station was set up in the downstream of each tributary, and the monthly concentration of  $\rm NH_4^+$  and TP was monitored from 2002 through 2011.

Six sampling stations were selected covering Lake Chaohu. Sampling stations S1–S4 were located in the western lake, while S5 and S6 were located in the eastern



**Fig. 1** Sampling stations set up in tributaries and Lake Chaohu (S1–S6). DR: Diaubu River, ER: Ershibu River, NFR: Nanfei River, SR: Shinuli River, PR: Pai River, FLR: Fengle River, HBR: Hangbu River, ZR: Zhao River.

lake. Station S2 is near SR, S3 is near PR, and S5 is near ZR. The concentrations of TN, TP, and Chl-*a* in the six sampling stations were monitored monthly during 2001 through 2011 to investigate the dynamics of water quality.

#### 1.2 Sampling and analytical methods

Surface water samples were collected using a Niskin water sampler. At each sampling occasion, a portion of the water samples was preserved in brown glass bottles (500 mL) with  $H_2SO_4$  solution (the final pH of water sample < 2) for the determination of TN, TP and COD<sub>Mn</sub>; part of the water samples was filtered through a 0.45 µm glass fiber filter and preserved in 50 mL plastic bottles for the determination of NH<sub>4</sub><sup>+</sup>; additionally, a 1-L water sample was filtered through a 0.45-µm glass fiber filter, after which the glass fiber with filtered phytoplankton was preserved for the determination of Chl-*a*. All samples were preserved at 4°C and analyzed in the lab within 24 hr.

The TN and TP concentrations were determined using the alkaline potassium persulfate digestion-UV spectrophotometric method. The ammonium nitrogen concentration was determined using the colorimetric method. Chl-*a* was calculated from spectrophotometric measurements after extraction in hot 90% ethanol. The COD<sub>Mn</sub> concentration was determined using the standard titrimetric method; pH, water temperature, electrical conductivity and dissolved oxygen (DO) were measured by using portable meters during sampling.

## **1.3** Calculation of total water discharge of the eight studied tributaries

The total water discharge of the eight studied tributaries was estimated using rainfall data and the runoff coefficient within the watershed. The monthly rainfall ranged between 3.5 and 304.2 mm (**Fig. 2**). The many-years' mean runoff coefficient was about 0.46 within the watershed (Yang and Zhang, 2005; Gao et al., 2009). Then we calculated that the total water discharge to the lake would range from  $33.7 \times 10^8$ –46.0 × 10<sup>8</sup> m<sup>3</sup> with a mean value of 39.6 × 10<sup>8</sup> m<sup>3</sup> during 2002–2011. This result is very close to the monitored value in other reports (40 × 10<sup>8</sup> m<sup>3</sup>, Mi and Zhou, 2009). Considering the water discharge of the eight tributaries to Lake Chaohu (about 90%), it is estimated that about  $30.3 \times 10^8$ –41.4 × 10<sup>8</sup> m<sup>3</sup> water was discharged to the lake during the study period.

#### 1.4 Statistical analysis

Statistical analysis was done using the SPSS 17.0 software package. One-way ANOVA (LSD test) and Independent-Samples *t*-Test at the 0.05 confidence level were conducted to test the difference between group mean values. Two-tailed Pearson correlation analysis was carried out to illustrate the correlative relationships between water parameters.

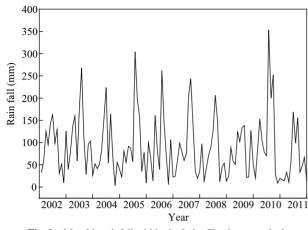


Fig. 2 Monthly rainfall within the Lake Chaohu watershed.

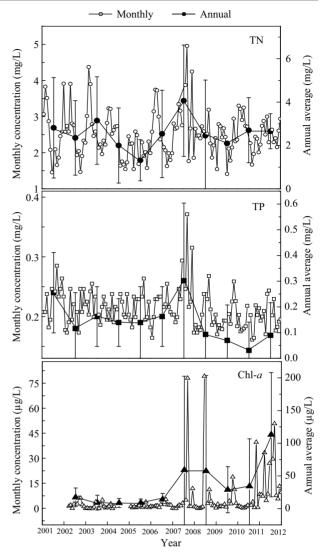
#### 2 Results and discussion

## 2.1 Temporal and spatial changes of TN, TP, and Chl-*a* in Lake Chaohu

Concentrations of TN, TP, and Chl-a in all water samples ranged 0.13-14.60 mg/L (maximum in S2, August 2007), 0.03-1.08 mg/L (maximum in S1, August 2005), and 0.10-465.90 µg/L (maximum in S2, June 2008) (Fig. 3), respectively. The annual mean concentration of TN, TP, and Chl-a ranged from  $1.79 \pm 0.57$  to  $3.44 \pm 1.54$  mg/L,  $0.14 \pm 0.04$  to  $0.26 \pm 0.15$  mg/L, and from  $3.19 \pm 2.70$  to 44.16  $\pm$  37.23 µg/L, respectively, and no clear temporal trends for the three water parameters were observed. However, seasonality analysis showed that TN exhibited the highest level in spring with a range of 2.76-3.40 mg/L and the lowest level in autumn with a range of 2.33-3.24 mg/L (Fig. 4). For TP and Chl-a, the highest level were both observed in summer with a range of 0.21-0.24 mg/L and 14.74-46.26 µg/L, respectively. According to the classification of water parameters by the Environmental Quality Standards for Surface Water promulgated by the Chinese government, the water quality of Lake Chaohu was classified as grade III to V during the study period.

The mean concentrations of TN, TP, and Chl-*a* in the western lake (station S1–S4) were  $3.05 \pm 1.73$  mg/L,  $0.22 \pm 0.12$  mg/L, and  $18.83 \pm 50.34$  µg/L; the values for the eastern lake (station S5, S6) were  $1.24 \pm 0.70$  mg/L,  $0.11 \pm 0.06$  mg/L, and  $3.26 \pm 5.31$  µg/L (**Fig. 5**), respectively. The Independent-Samples *t*-Test showed that the mean concentrations of TN, TP, and Chl-*a* in the western lake were significantly higher than those in the eastern lake ( $\alpha = 0.05$ , p < 0.01), which indicates a clear spatial distribution of the three parameters in this lake.

The correlative relationships between environmental variables were analyzed. Results showed that Chl-*a* was significantly positively correlated with electrical conductivity,  $COD_{Mn}$ , TN, and water temperature while negatively correlated with pH, DO, and TP (**Table 1**). This has been reported in other lakes (Chen et al., 2003).



1119

Fig. 3 Temporal changes of TN, TP, and Chl-a in Lake Chaohu, data are presented as mean  $\pm$  SD.

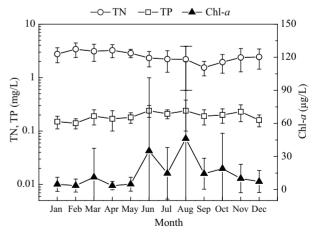


Fig. 4 Seasonal changes of TN, TP, and Chl-a in Lake Chaohu, data are presented as mean  $\pm$  SD.

Lake eutrophication accompanying economic development is a universal problem in China (Chen et al., 2003;

Journal of Environmental Sciences 2013, 25(6) 1117-1123 / Libiao Yang et al.

	Table 1	Table 1 Constantion coefficient between environmental variables in Lake Chaonu (Fearson, 2-taneu)						
Variables	pН	Electrical conductivity	DO	COD <sub>Mn</sub>	TN	TP	Water temperature	Chl-a
pН	1.00							
Electrical conductivity	-0.59	1.00						
DO	0.63	-0.85	1.00					
COD <sub>Mn</sub>	0.02	-0.11	0.28	1.00				
TN	0.35	-0.25	0.54	0.46	1.00			
TP	0.37	0.66	0.88	0.39	0.54	1.00		
Water temperature	-0.40	0.66	0.63	0.15	-0.34	-0.48	1.00	
Chl-a	-0.03	0.17	-0.09	0.48	0.24	-0.03	0.21	1.00

 Table 1
 Correlation coefficient between environmental variables in Lake Chaohu (Pearson, 2-tailed)

Data in bold font mean that the correlation is significant at 0.015 level.

Xia et al., 2011). Our monitoring data showed relatively high nitrogen and phosphorus levels and a highly eutrophic condition in Lake Chaohu; this indicates that the water quality of this lake was not substantially improved. In this study, higher level water parameters in the lake were observed in 2007 and 2008, and this may be caused by the longer stagnation time of nutrients resulting from the lower precipitation during those two years (Fig. 2). Additionally, the highest Chl-a content was observed in 2011, meaning excessive phytoplankton growth was stimulated due to the long-term presence of higher nitrogen and phosphorus concentrations. For example, it has been recorded that a total of 28 algal species belonging to 5 phyla were identified during 2001-2005 in this lake (Zhang, 2007). However, 48 algal species belonging to 6 phyla have been identified recently (Yang et al., 2011). Lake Taihu, another shallow lake of China, became famous because of its highly eutrophic condition, and the dynamics of nutrients in this lake has been well studied. In our estimation, these two eutrophic lakes showed a different pollution character. Over the recent decades, the TN concentration in Lake Taihu showed an increasing trend and the many year's mean concentration (mean 2.34 mg/L) was the same to the value observed in Lake Chaohu (mean 2.34 mg/L); while the TP concentration (mean 0.176 mg/L) was lower than our monitored data in Lake Chaohu (mean 0.20 mg/L) (Zhu, 2008). This is due to the fact that, in addition to the nutrients exported from urban wastewater and agricultural runoff, a stratum enriched with phosphorite is located in the Lake Chaohu basin, which would significantly contribute phosphorus to the lake water due to land runoff and erosion.

#### 2.2 Dynamics of eutrophication in Lake Chaohu

The annual mean ratio of TN:TP by weight ranged between 10 and 20 in Lake Chaohu during the study period and was higher than the Redfield ratio of 7:1 (Redfield, 1958) (**Fig. 6**), indicating that phosphorus was the limiting nutrient in this lake. This is consistent with the reports that freshwater ecosystems are mainly phosphorus-limited (Capblancq, 1990), though nitrogen limitation was observed in other lakes (Camacho et al., 2003; May et al., 2010). In addition, the ratio of TN:TP in the lake showed a decreasing trend over 2001–2005 while a increasing trend was seen over 2005–2011.

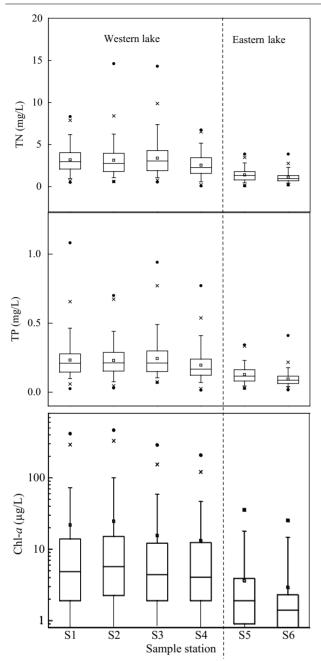
The long-term dynamics of eutrophication in Lake Chaohu are shown in **Fig. 7**. Here a Chinese trophic classification system for lakes was selected (Zhang et al., 1999), in which five trophic conditions from oligotrophic to ultraeutrophic were assigned according to TP versus Chl-*a* content level. The results showed that Lake Chaohu was ultra-eutrophic during the study period. When the trophic condition was assessed according to the classification proposed by Forsberg and Ryding (1980) we also found that Lake Chaohu was hypertrophic over 2001 to 2011. This result indicates that eutrophication in Lake Chaohu was not substantially controlled during recent years (Shang and Shang, 2007).

In this study, a similar seasonality variation for TP and Chl-*a* was observed in this lake. This is consistent with the reports by Hofmann et al. (2011) that the Chl-*a* concentration in the mixed water was often dependent on nutrient limitations. The seasonality variation of Chl-*a* (peak at summer season) in Lake Chaohu may be related to the change of biomass of algal species, and this has been proved by previous studies. Jiang et al. (2010) had reported that the Chl-*a* concentration in Lake Chaohu was significantly related to the biomass of *Microcystis*, which tends to be at a maximum in summer.

#### 2.3 Impact of riverine nutrient loading on lake water quality

Total phosphorus and  $NH_4^+$  loading to Lake Chaohu from the eight major tributaries was calculated using the data of total water discharge and annual mean nutrient concentrations, through which the impact of riverine nutrient loading on lake water quality was expected to be well understood. Monitoring data showed that the annual mean concentration (calculated based on the monthly data) of TP and  $NH_4^+$  in river water ranged from 0.04 (Fengle) to 2.08 mg/L (Shiwuli) and 0.18–58.81 mg/L (Shiwuli) (**Fig. 8**), respectively, and the overall mean concentrations of TP and  $NH_4^+$  in Shiwuli, Dianbu, and Ershibu was significantly higher than in other rivers ( $\alpha = 0.05$ , p <0.001). The concentration of TP (1.08 mg/L) and  $NH_4^+$ (11.83 mg/L) in Nanfei in 2002 was significantly higher

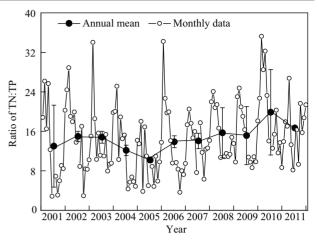
Vol. 25



**Fig. 5** Spatial distribution of TN, TP and Chl-*a* in Lake Chaohu. The box plot shows the 10th and 90th percentiles, the median and mean, and the 25th and 75th percentiles.

than the subsequent six years ( $\alpha = 0.05$ , p < 0.001).

Taking the parameter of total water discharge into consideration, it is estimated that about  $0.19 \times 10^4$ –0.27 ×  $10^4$  tons TP (mean  $0.27 \times 10^4$  tons) and  $4.17 \times 10^4$ –5.47 ×  $10^4$  tons NH<sub>4</sub>+(mean  $4.35 \times 10^4$  tons) was exported to the lake over 2002–2011 (**Fig. 9**). The water environment capability of TP and NH<sub>4</sub>+ in Lake Chaohu (calculated based on the Grade-III water quality) ranged from 0.05 ×  $10^4$ –0.06 ×  $10^4$  and  $1.01 \times 10^4$ –1.27 ×  $10^4$  tons/yr during the study period (unpublished data), respectively. Thus it is clear from the data that the riverine nitrogen



1121

Fig. 6 Ratios of TN:TP by weight in Lake Chaohu during 2001 through 2011. Annual mean data are presented as mean  $\pm$  SD.

and phosphorus loading exceeded the water environment capability of the two nutrients by a factor of 3–6.

Considering that lake sediments always have significant impacts on lake water quality (Zhang et al., 1999), we conducted an in situ measurement in 2008 to investigate the benthic fluxes of dissolved inorganic nitrogen and phosphorus in Lake Chaohu (12 sampling sites covering the lake) to estimate the internal loads of nutrients. The results showed that the mean benthic flux of NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, and  $PO_4^{3-}$  was 3.56 ± 1.52 mg N/(m<sup>2</sup>·day), -0.14 ± 0.40 mg N/(m<sup>2</sup>·day), and  $-1.54 \pm 21.94$  mg P/(m<sup>2</sup>·day) (unpublished data), respectively. When taking the parameter of sediment area of the lake into consideration, it is estimated that approximately 925 tons nitrogen was released to the water column from lake sediments while 0.87 tons water phosphorus was consumed by sediments on a whole lake basis. Compared to the contribution of external loads estimated in this article, this strongly indicates that riverine nutrient loading is mainly responsible for the eutrophication in Lake Chaohu. Thus, reduction of nutrient loads in the sub-watershed and tributaries would be essential for the

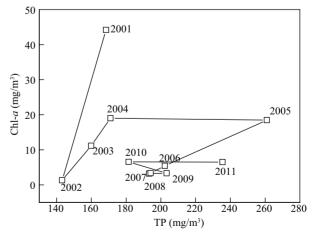


Fig. 7 Long-term dynamics of eutrophication in Lake Chaohu during 2001 through 2011.

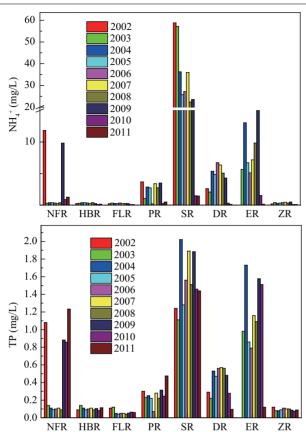


Fig. 8 Monthly concentration of  $NH_4^+$  and TP in eight tributaries during 2002 through 2011.

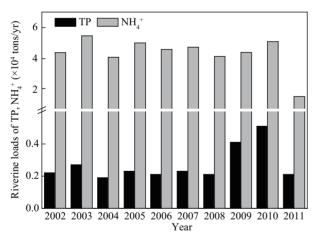


Fig. 9 Riverine nutrient exports to Lake Chaohu during 2002 through 2011.

restoration of this lake.

#### **3** Conclusions

Lake Chaohu was highly eutrophic and water quality showed no substantial improvement during 2001 through 2011. Significantly higher concentrations of TN, TP, and Chl-*a* were observed in the western lake indicating significant spatial variation in Lake Chaohu. The annual mean

ratios of TN:TP by weight were higher than 7:1 during the study period meaning phosphorus was the limiting nutrient in the lake. Riverine TP and  $NH_4^+$  loading from eight tributaries far exceeded the water environment capability and the amount contributed by internal loads indicating that nutrient exports from the tributaries play the most crucial role in water eutrophication. Thus reduction of nutrients loading in the sub-watershed and tributaries is essential for the restoration of Lake Chaohu.

#### Acknowledgments

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