Seasonal Pattern of Nutrient Limitation in a Eutrophic Lake and Quantitative Analysis of the Impacts from Internal Nutrient Cycling

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S Supporting Information

ABSTRACT: Nutrient dynamics in lakes are determined by the external anthropogenic discharges and unobserved internal cycling processes. In this work, a decadal nutrient data set from the eutrophic Lake Taihu, China, revealed a strong seasonal pattern of nutrient concentration and limitation. A nutrient-driven dynamic eutrophication model based on a Bayesian hierarchical framework was established to quantify the relative contributions to temporal variations from external discharges and internal processes. Results showed that after years of efforts on nutrient reduction, external discharges were relatively small and fluctuated less between seasons compared to the internal processes. A quantitative relationship between monthly nutrient concentration and corresponding internal loading was observed. Lake sediment could transform from a source of phosphorus in overlying water in summer and autumn to a sink in winter and spring. Together with temporal variations in nitrification and denitrification, seasonal transformation from the limitation of phosphorus induced colimitation of nitrogen and phosphorus. Understanding the potential impact of internal nutrient cycling on a seasonal pattern of nutrient concentration and limitation, the growth of phytoplankton, and, possibly, phytoplankton community composition should be emphasized, given the change in the relative importance of external discharges and internal loading in the process of lake restoration.
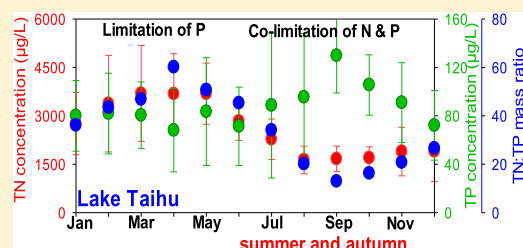
INTRODUCTION

The water supply crisis and water pollution control are some of the greatest challenges that threaten the sustainable development of human society worldwide.[1,2] Eutrophication, primarily induced by nutrient enrichment, and subsequent occurrences of harmful algal blooms (HABs) in aquatic systems have become a major water quality problem globally.[3−6] Since the 1990s, water quality has deteriorated in many rivers and lakes in Africa, Asia, and Latin America.[7] According to the data from the United Nations Environment Programme, over 75% of the closed water bodies (e.g., reservoirs and lakes) in the world have experienced a certain degree of eutrophication.[8] In freshwater ecosystems, there is an unprecedented increase in the occurrences of HABs.[8] These blooms have direct economic impacts and affect ecosystem functioning.[9] For instance, microcystins produced by *Microcystis* spp. and *Planktothrix* spp. could have serious toxic effects on humans and aquatic animals,[10] influence food web structures, and result in biodiversity loss.[4] In China, many lakes and reservoirs have become or are becoming eutrophicated since the early 2000s[11] due to the intensification of anthropogenic nitrogen (N) and phosphorus (P) discharges.[12,13]

Reducing anthropogenic N and P discharges in watersheds is usually the focus of mitigation measures to improve water quality.[14] Despite continuous reduction of external nutrient discharge, improvement of water quality in eutrophic lakes was usually slower than previously expected.[1,11,15] Increasing evidence has suggested that internal nutrient loading is an important factor in maintaining eutrophication in lakes and that it prevents rapid improvements in water quality.[16,17] During the heavy loading periods, N and P could accumulate in lake sediments, but they could be released into overlying water with reductions of external discharge.[18] Nutrients
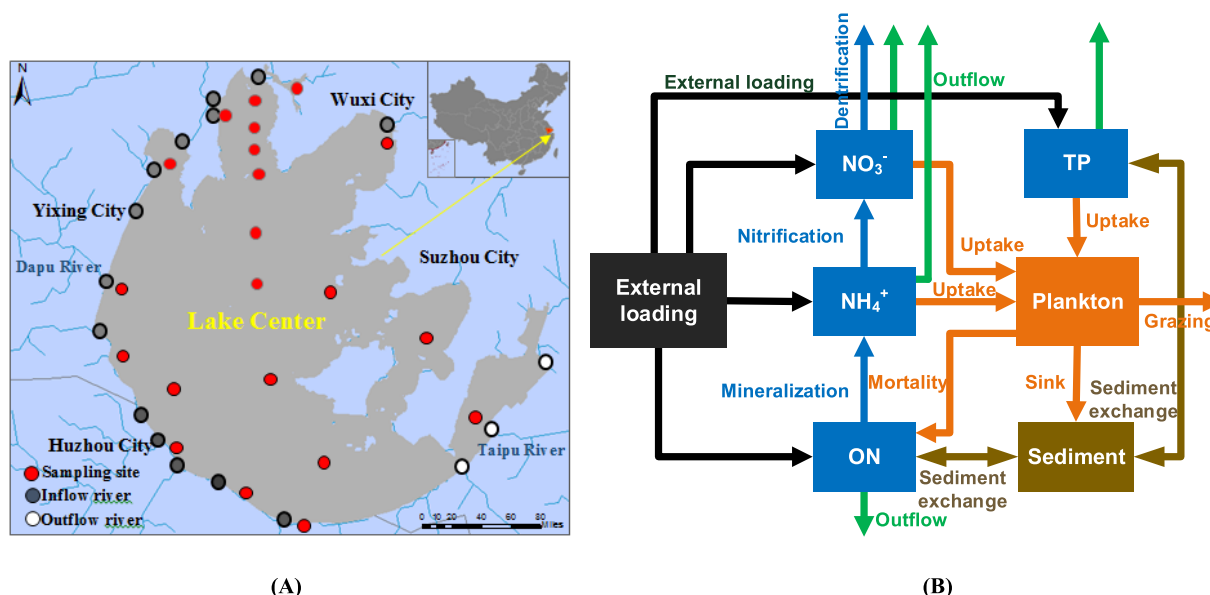
Figure 1. Location of nutrient monitoring sites in Lake Taihu, and its inflow and outflow rivers (A) and major processes involved in the in-lake dynamic modeling (B).

contributed by sediment release could account for a substantial part of the total nutrient discharge into the lake, sometimes even exceeding the external discharge.[19] Driven by a combination of external discharge and internal processes, many freshwater systems are facing temporal alterations in nutrient concentration and ratio.[20,21] These shifts might bring some unexpected ecological consequences to the aquatic system, such as favoring some algal species with stronger competitive abilities for using P[22] and increasing the per-cell production of toxins by such species.[10]

Internal loadings in lakes are difficult to quantify using field monitoring, and it is complicated to hindcast the historical cycling processes either.[23−25] Based on the existing knowledge of biogeochemical processes, nutrient-driven dynamic biogeochemical models have been applied to characterize temporal variations of internal cycling processes.[26,27] Parameter estimation and uncertainty analysis in the modeling could be accomplished by framing implicit assumptions into equations and using a Bayesian inference.[26−28] This method could provide more realistic estimates of the existing knowledge and predictive uncertainty by taking into account both uncertainties regarding parameters and that which remains when the parameters are known.[27] Markov chain Monte Carlo samples are taken from a posterior distribution; therefore, the procedure works for all sample sizes and various sources of non-normality.[23] Nutrient-driven dynamic biogeochemical models have been successfully applied to characterize the biogeochemical processes in aquatic systems, such as the dynamics of phytoplankton growth in the Neuse River Estuary, United States,[27] and in the Gulf of Gera, Greece;[29] the response of freshwater organisms to different environmental drivers in the Taizi River, China;[30] and the contributions of different internal cycling processes to temporal nutrient variations in Lake Yilong[31] and Lake Dianchi in China.[23]

Lake Taihu, the third largest freshwater lake in China (with an area of 2338 km^2),[20] is located at the lower Yangtze River Basin. The surrounding watershed is one of the most densely populated (accounting for about 4.4% of the national

population) and developed regions (accounting for about 10% of the national gross domestic product) in China.[32,33] Lake Taihu is an important source of drinking water for the 20 million inhabitants in the cities of Wuxi and Suzhou.[32] In the 1960s, it was a diatom-dominated meso-oligotrophic lake that transformed into a eutrophic, cyanobacteria-dominated system after 2000, with blooms occurring regularly from spring to late fall.[34] In May 2007, an outbreak of HABs in Lake Taihu overwhelmed a waterworks that supplies Wuxi city, leaving over 2 million residents without drinking water for a week.[35] This crisis initiated the efforts to reduce anthropogenic nutrient discharge and improve lake water quality. So far, most efforts have been devoted to reductions of external nutrient discharge.[32,36] For instance, the number of wastewater treatment plants in the watershed increased from 139 to 244 between 2007 and 2016, with wastewater treatment capacity increasing from 3.23 to 8.48 million tons per day.[37] Over 3000 domestic wastewater treatment facilities were constructed in the rural region.[37] These measures have cost about 100 billion Chinese yuan (equivalent to about U.S. $14.5 billion).[37] However, nutrient concentrations and occurrences of HABs in Lake Taihu have not decreased as expected, given the continuous abatement efforts and the huge investment into the same.[32,36−38]

After years of efforts on reduction of external discharge in Lake Taihu, several key questions have been raised during attempts on lake restoration: (I) Are there any temporal variations in nutrient concentration or limitation? (II) How much do different internal processes and external discharge contribute to these temporal variations? (III) How do different internal processes alter between seasons? What are their potential impacts on aquatic systems? Based on a decadal nutrient monitoring data set between 2007 and 2016, we characterized seasonal patterns of typical nutrient concentrations and their ratios in Lake Taihu, and explored the potential driving forces for temporal patterns. A nutrient-driven dynamic biogeochemical model based on a Bayesian hierarchical framework was established to quantify relative contributions of external discharge and different internal

processes on a temporal timescale. Evidence from a eutrophic lake with many years of efforts on restoration could help water managers to rethink the existing restoration measures and reconsider the potential impacts of internal cycling processes for improvement of water quality, growth of phytoplankton, and, possibly, alteration of their community composition.

■ MATERIALS AND METHODS

Lake Description and Field Monitoring Data. Lake Taihu is located in the southeastern part of the Yangtze River Basin, China (30°55′40″−31°32′58″N; 119°52′32″−120°36′10″E) (Figure 1A). It is a subtropical, shallow, and well-mixed eutrophic lake,[39] with an area of 2340 km², a watershed area of 36 500 km², an average depth of 2.1 m, and a water volume of 4.4 billion m³.[40] Lake Taihu has 22 major inflow rivers or tributaries and an annual freshwater input of 88 × 10⁸ m³.[41] In this study, the nutrient monitoring data set consists of monthly nutrient monitoring data in the lake and major inflow and outflow rivers from January 2007 to December 2016 (Figure 1A). Nutrient data for the inflow and outflow rivers were used to estimate the nutrient input to or output from Lake Taihu, whereas data for the lake were used to reveal the in-lake nutrient dynamics during the study period. Nutrients in the data set include total nitrogen (TN), total phosphorus (TP), ammonia (NH_4^+−N), nitrate (NO_3^-−N), organic nitrogen (ON), and chlorophyll a (Chl a). TN, TP, and Chl a data in the rivers and Lake Taihu were obtained from the regular water quality monitoring program by the Ministry of Ecology and Environment, China; the corresponding NH_4^+−N, NO_3^-−N, and ON data were obtained from the Lake-Watershed Science Data Center, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences. A total of 21 monitoring sites were set in the center, deep zone, and shore zones of Lake Taihu (Figure 1A). Procedures for collecting water samples were based on the "Technical Specifications Requirements for Monitoring of Surface Water and Waste Water in China." External nutrient discharges through inflow and outflow rivers of Lake Taihu were estimated based on the monthly nutrient concentrations and corresponding runoff. The calculated results are shown in Figure S1. Runoff data for these rivers were obtained from the Ministry of Water Resources, China.[42]

In this study, TN concentration was determined by persulfate digestion, followed by automated colorimetric analysis [N-(1-naphthyl)ethylenediamine dihydrochloride spectrophotometry], with a method detection limit (MDL) of 50 μg·L⁻¹.[43] TP concentration was determined by persulfate digestion, followed by automated colorimetric analysis (ammonium molybdate and antimony potassium tartrate under acidic conditions), with an MDL of 10 μg·L⁻¹.[44] Chl a concentration was determined by acetone extraction, followed by centrifugal separation and determination of sample absorbance, with an MDL of 1 μg·L⁻¹.[45] NH_4^+−N concentration was determined by flow injection analysis and salicylic acid spectrophotometry, with an MDL of 10 μg·L⁻¹.[46] NO_3^-−N concentration was determined by gas-phase molecular absorption spectrometry, with an MDL of 6 μg·L⁻¹.[47]

Modeling Seasonal Dynamics of Internal Cycling Processes. To reveal dynamic relationships between nutrients and phytoplankton growth, a nutrient-driven dynamic biogeochemical model based on a Bayesian hierarchical framework was established, with the structural framework shown in Figure 1B. This model relates phytoplankton's growth with external nutrient discharge and major internal nutrient cycling processes in Lake Taihu. Based on the Liebig law of the minimum,[48] growth of phytoplankton was assumed to be affected by the multiplication of the N and P limiting factors.[23] The sinking and mortality of phytoplankton were described as first-order processes.[23] The grazing of zooplankton was a quadratic process.[29] N cycling processes in Lake Taihu involved in the model included external discharge, mineralization of ON, nitrification of NH_4^+−N, denitrification of NO_3^-−N, phytoplankton uptake of NH_4^+−N and NO_3^-−N, ON exchange between overlying water and sediment, and outflow discharge (Figure 1B). P cycling processes involved external discharge, uptake by phytoplankton, P exchange between overlying water and sediment, and outflow discharge. Particle-bound and dissolved P was not differentiated due to the lack of monitoring data. Because Lake Taihu is a shallow and well-mixed lake,[39] it is treated as a whole without addressing spatial variances in this study. However, in fact, in the east part of Lake Taihu, there are still some areas of macrophytes distributed at the shores or in the bays.[49,50] Previous studies reported that nutrient inputs into Lake Taihu through groundwater[51] and atmospheric deposition[38] were relatively low (usually less than 10%) compared with riverine discharge. Therefore, these processes were not included in the model. The main equations involved in the model were listed as follows[23]

$$\frac{dB}{dt} = \left(M \times f_N \times f_P - \text{mo} - \frac{\text{vs}}{h} \right) \times B - G_L \times B^2 - \frac{Q}{V} \times B \tag{1}$$

$$\frac{d(NH_4^+)}{dt} = \frac{L_{NH}}{V} + a \times (ON) - \text{ni} \times (NH_4^+) - \frac{(NH_4^+)}{(NH_4^+) + (NO_3^-)} \times M \times f_N \times f_P \times r_1 \times B - \frac{Q}{V} \times (NH_4^+) \tag{2}$$

$$\frac{d(NO_3^-)}{dt} = \frac{L_{NO}}{V} - \text{de} \times NO_3 + \text{ni} \times (NH_4^+) - \frac{(NO_3^-)}{(NH_4^+) + (NO_3^-)} \times M \times f_N \times f_P \times r_2 \times B - G_L \times B^2 - \frac{Q}{V} \times (NO_3^-) \tag{3}$$

$$\frac{d(ON)}{dt} = \frac{L_{ON}}{V} + r_3 \times \text{mo} \times B + S_N \times (ON) - a \times (ON) - \frac{Q}{V} \times (ON) \tag{4}$$

$$\frac{d(TP)}{dt} = \frac{L_P}{V} + S_P \times (TP) - \frac{Q}{V} \times (TP) \tag{5}$$

where B is the phytoplankton biomass (g·C·m⁻³); M is the maximum growth rate of biomass (day⁻¹); f_N and f_P are the N and P limiting factors (unitless); mo is the phytoplankton mortality rate (day⁻¹); vs is the sinking velocity of phytoplankton (m·day⁻¹); h is the depth of the lake (m); G_L is the grazing loss rate by zooplankton [m³·(g·C·day)⁻¹]; Q is

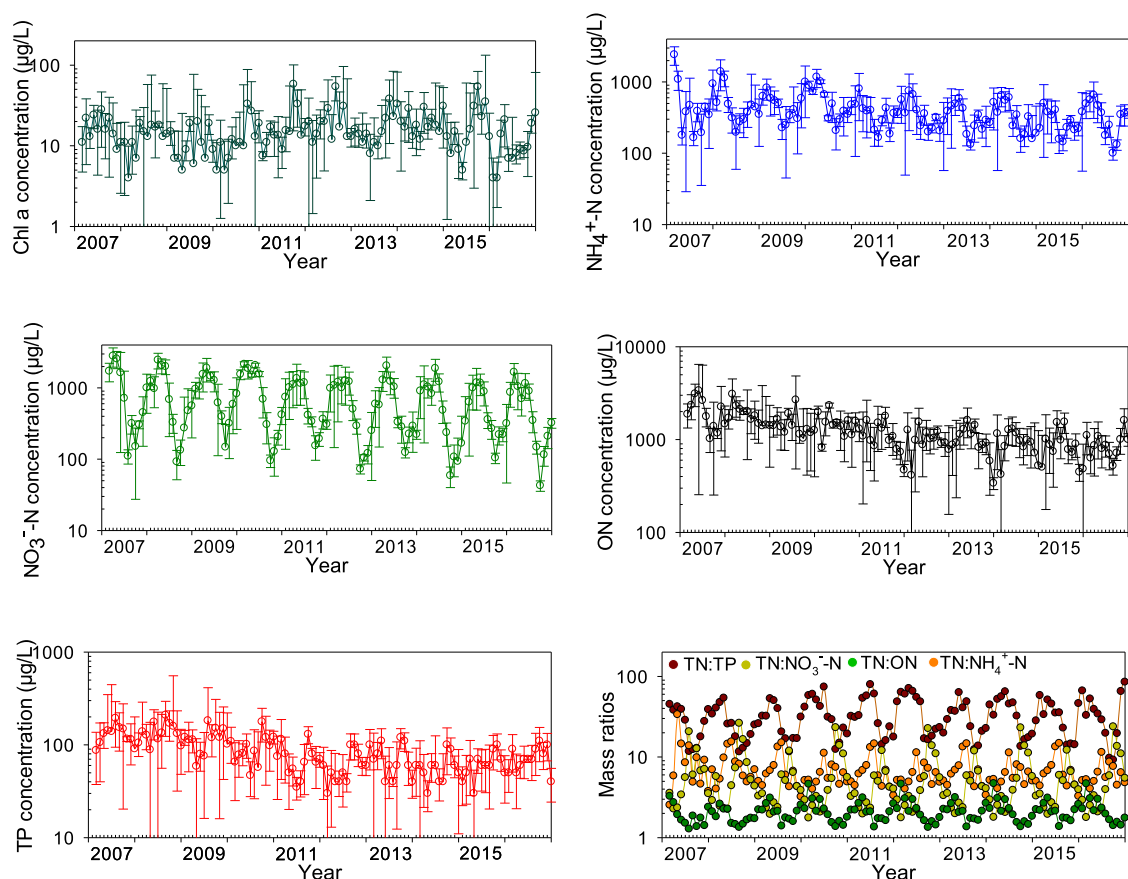**Figure 2.** Seasonal variations of chlorophyll a (Chl a), ammonia (NH_4^+-N), nitrate (NO_3^--N), organic nitrogen (ON), and total phosphorus (TP) concentrations and their ratios (TN/TP, TN/NH_4^+-N, TN/NO_3^--N, and TN/ON) in Lake Taihu between 2007 and 2016.

the outflow rate from the lake ($m^3 \cdot day^{-1}$); V is the water volume in Lake Taihu (m^3); L_{NH}, L_{NO}, L_{ON}, and L_P are the respective external NH_4^+-N, NO_3^--N, ON, and TP discharges into the lake ($g \cdot day^{-1}$); a is the mineralization rate of ON (day^{-1}); ni is the nitrification rate of NH_4^+-N (day^{-1}); r_1 is the NH_4^+-N/C ratio in the phytoplankton (unitless); de is the denitrification rate of NO_3^--N (day^{-1}); r_2 is the NO_3^--N/C ratio in the phytoplankton (unitless); r_3 is the ON/C ratio in the phytoplankton (unitless); S_N and S_P are the sediment exchange rates for ON and TP, respectively (day^{-1}). f_N and f_P were calculated based on the nutrient concentrations and Michaelis−Menten constant for N and P, respectively (unitless). The detailed values or distributions of the selected parameters in the models are provided in Table S1. In summary, eq 1 is used to describe the processes that influence the growth of phytoplankton; eqs 2−5 are used to describe the processes that influence NH_4^+-N, NO_3^--N, ON, and TP concentrations in the overlying water. In temporal dynamic simulations, each year is divided into four subperiods based on the seasonal pattern of water temperature and solar radiation in the watershed (spring: February, March, and April; summer: May, June, and July; autumn: August, September, and October; winter: November, December, and January). Each subperiod is treated as a submodel in the dynamic modeling.

A Bayesian hierarchical framework[28] is used for estimation of five key parameters, including the growth rate of phytoplankton (M), sediment P exchange rate (S_P), sediment N exchange rate (S_N), NO_3^--N denitrification rate (de), and NH_4^+-N nitrification rate (ni). M_i, S_{Pi}, S_{Ni}, d_{ei}, and n_{ii} were the equivalent parameters in each submodel. They obeyed the

normal distributions as follows: $M_i \sim N (m_M, \sigma_M)$, $S_{Pi} \sim N (m_{SP}, \sigma_{SP})$, $S_{Ni} \sim N (m_{SN}, \sigma_{SN})$, $d_{ei} \sim N (m_{de}, \sigma_{de})$, and $n_{ii} \sim N (m_{ni}, \sigma_{ni})$. m_M, m_{SP}, m_{SN}, m_{de}, and m_{ni} were global parameters for M, S_P, S_N, de, and ni. σ_M, σ_{SP}, σ_{SN}, σ_{de}, and σ_{ni} were their corresponding standard deviations. Prior distributions for these five global parameters have been summarized by previous studies as follows: $m_M \sim N (1.5, 1.0)$,[52] $m_{SP} \sim N (0.0, 0.02)$,[23,32] $m_{SN} \sim N (0.0, 0.02)$,[23] $m_{de} \sim N (0.1, 0.1)$,[53] and $m_{ni} \sim N (0.1, 0.1)$.[54] Their standard deviations were estimated with priors as follows:[23,52] $\sigma_M \sim N (1.0, 1.0)$, $\sigma_{SP} \sim N (0.1, 0.1)$, $\sigma_{SN} \sim N (0.1, 0.1)$, $\sigma_{de} \sim N (0.1, 0.1)$, and $\sigma_{ni} \sim N (0.1, 0.1)$. Markov chain Monte Carlo samples are taken from the posterior distributions, and as a result, this procedure works for all sample sizes and various sources of non-normality.[26,55] The sampling is implemented in the Win-BUGS (version 1.4.3) differential interface, and it was carried out by using three chains, each with 1000 iterations. The accuracy of posterior estimates was confirmed by requiring that the Monte Carlo error for all parameters was less than 10% of the sample standard deviation. As in previous studies,[23,27,31] the model's fitting performance is evaluated by comparing the calculated results with the monthly monitored results through the root-mean-squared error (RMSE) and coefficient of determination (R).

To address potential impacts from internal processes on future improvement of water quality in Lake Taihu, three scenarios with different strategies of reduction in external discharge are simulated. Their responses to Chl a and nutrient concentrations are estimated. Rates in internal cycling processes (e.g., denitrification, nitrification, and sediment
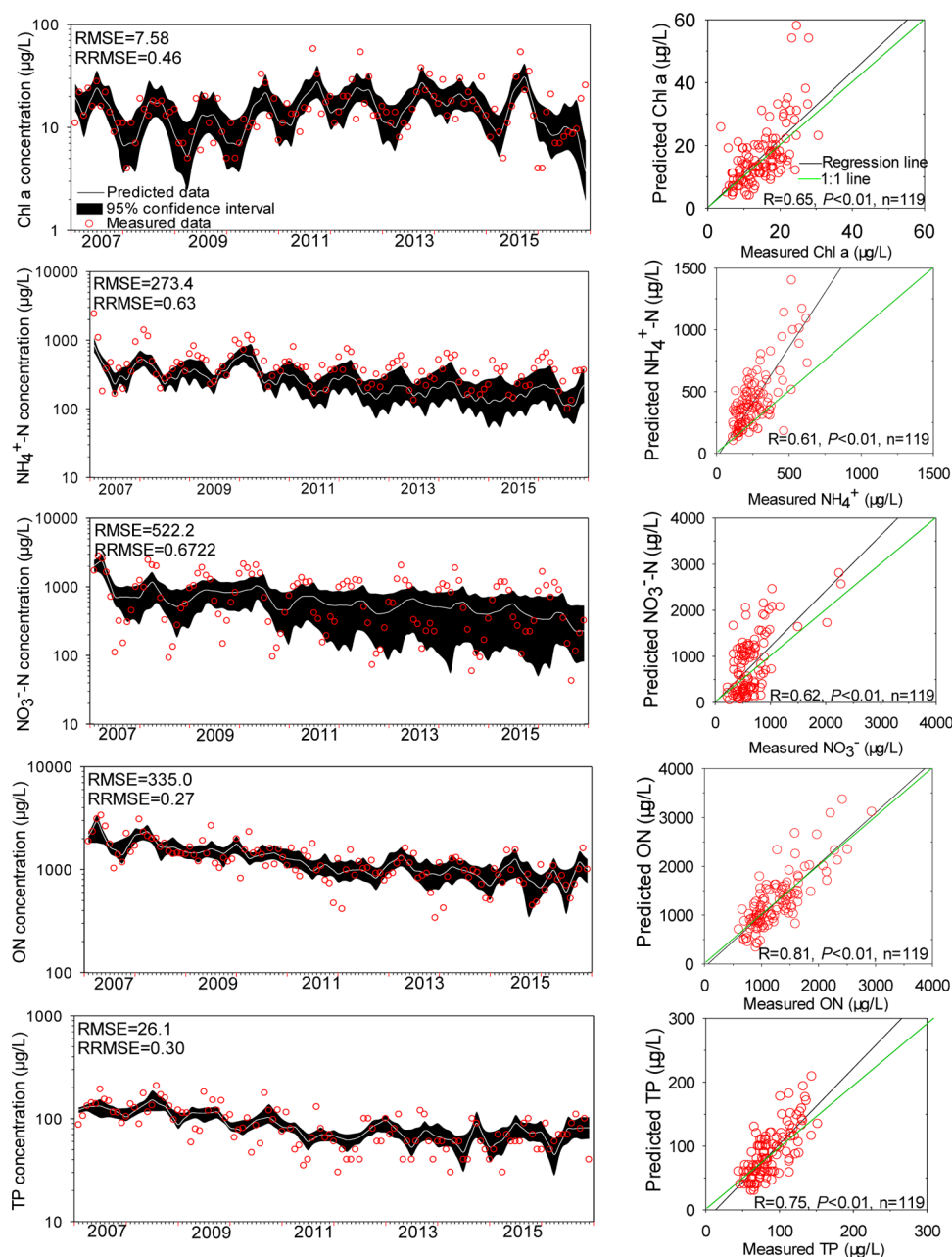
Figure 3. Model's prediction results and comparison with the monitoring data. The red dots represent the monthly field monitoring results.

exchange) in 2016 are used as the initial inputs. In the baseline scenario, external nutrient discharge in 2016 is introduced as the model input and remains stable during a 10 year simulation; in scenarios I and II, a 50% reduction in external N and P discharge compared to that in 2016 is assumed after 10 years. In scenario I, a season-specific nutrient reduction strategy is simulated. That is, reduction of external P discharge is achieved in summer and autumn (summer: May, June, and July; autumn: August, September, and October), and reduction of external N discharge is achieved in spring and winter (spring: February, March, and April; winter: November, December, and January). In scenario II, reduction of external N and P discharge is achieved without seasonal differences.

■ RESULTS

Seasonal Pattern of Nutrient Concentration and Limitation in Lake Taihu. Nutrient concentrations in Lake

Taihu have shown strong seasonal patterns over a decade (Figures 2 and S2), although the amplitude of seasonal fluctuations partly depends on the detailed nutrient types. In 2016, the annual average TN and TP concentrations in Lake Taihu were 1980 ± 660 and 73.3 ± 21.4 $\mu g \cdot L^{-1}$, respectively, much higher than the grade III limit in China (used as a standard for a clean lake in China, 1000 $\mu g \cdot L^{-1}$ for TN and 50 $\mu g \cdot L^{-1}$ for TP). The higher concentrations of N species usually occurred in winter and spring, whereas the lower values were observed in summer and autumn (Figure 2). For $NO_3^- -N$, the peak usually occurred in early spring (with the maximum concentration of 1540 ± 640 $\mu g \cdot L^{-1}$ in March), and then decreased abruptly during May–September (with the minimum concentration of 110 ± 40 $\mu g \cdot L^{-1}$ in September). In contrast to the seasonal pattern of N species, TP concentrations in water columns displayed an opposite seasonal trend, with the higher concentration occurring in summer and
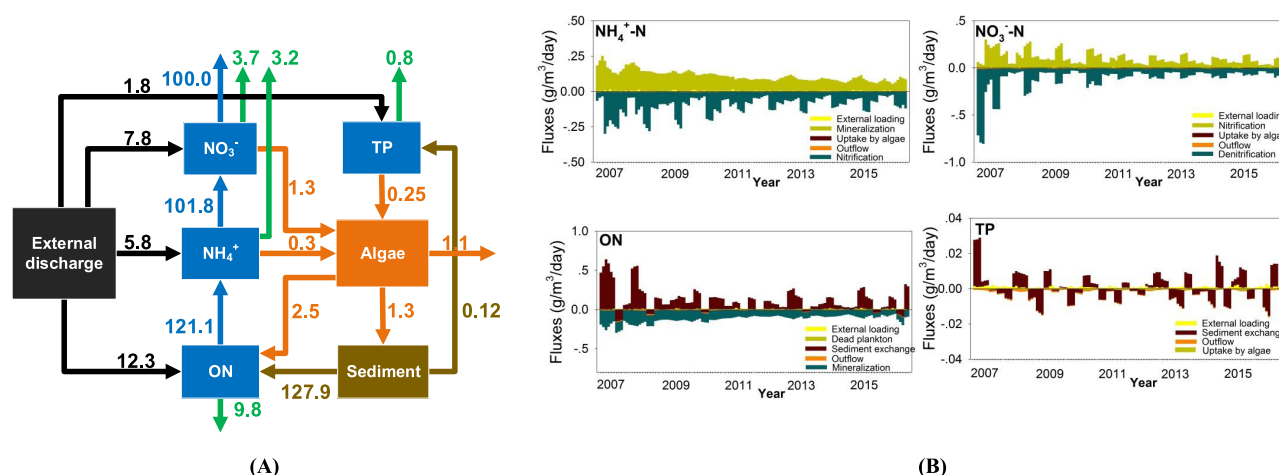
Figure 4. Nutrient cycling process in Lake Taihu in 2016 (Gg) (A) and major processes influencing water nutrient concentrations (B).

autumn (with a peak value of 130 ± 31 μg·L^{-1} in September) and the lower concentration in spring and winter (with a valley value of 68.1 ± 34.4 μg·L^{-1} in April). Chl a concentration in Lake Taihu (ranging from 11.0 ± 4.1 to 22.0 ± 17.0 μg·L^{-1}) also indicated recurring seasonal phytoplankton blooms, with maxima in summer.

TN/TP mass ratios in Lake Taihu showed strong seasonal patterns driven by the asynchronous alterations in nutrient concentrations (Figure 2). TN/TP ratios, which are important indices for predicting whether N or P is the limiting factor for the growth of phytoplankton in aquatic systems,[56] fluctuated significantly in Lake Taihu between seasons. In spring and winter, TN/TP mass ratios ranged from 32.2 ± 20.5 to 51.7 ± 9.8, but in summer, this value dropped below 20. In freshwater lakes, N-deficient phytoplankton growth was apparent at TN/TP mass ratios lower than 9; P-deficient growth occurred at TN/TP mass ratios higher than 23; at intermittent TN/TP ratios, either N or P can become deficient.[56] This fact indicates that the limiting nutrient in Lake Taihu was not consistent throughout the year. In spring and winter, P limitation occurs in Lake Taihu, but it transforms into a colimitation of both N and P in summer and autumn. Compositions of different N species in aquatic systems could also influence the growth of phytoplankton and their community compositions.[57] In Lake Taihu, strong seasonal patterns were observed for ratios between different N species. For instance, TN/NO$_3^-$−N ratios ranged from 2.4 ± 0.1 to 4.6 ± 0.9 during spring and winter but increased abruptly to 16.9 ± 0.5 in September (Figure S2).

Modeling Seasonal Nutrient Cycling Processes in Lake Taihu. A nutrient-driven dynamic biogeochemical model based on a Bayesian hierarchical framework was applied to characterize the seasonal dynamics of nutrient cycling process in Lake Taihu between 2007 and 2016. The model's performance was first evaluated by comparing the simulated monthly Chl a and nutrient concentrations with the field monitoring results in Lake Taihu (Figure 3). In general, the dynamic model could well reproduce the seasonal dynamics of nutrient concentrations; in particular, it successfully characterized the temporal peaks and valleys in 1 year. The RMSE and R between the predicted and the monitored values were 7.6 μg·L^{-1} and 0.65 ($P < 0.01$, $n = 119$, Pearson correlation) for Chl a, 273 μg·L^{-1} and 0.78 for NH$_4^+$−N ($P < 0.01$, $n = 119$), 522 μg·L^{-1} and 0.62 for NO$_3^-$−N ($P < 0.01$, $n = 119$), 335 μg·L^{-1} and 0.81 for ON ($P < 0.01$, $n = 119$), and 26.1 μg·

L^{-1} and 0.75 for TP ($P < 0.01$, $n = 119$), respectively (Figure 3).

This model showed the year-based fluxes in the different nutrient cycling processes that influence nutrient concentrations in Lake Taihu in 2016 (Figure 4A). In 2016, the riverine NH$_4^+$−N, NO$_3^-$−N, ON, and TP discharges into Lake Taihu were 5.8, 7.8, 12.3, and 1.8 Gg, respectively. A seasonal variation in nutrient inflows was observed, with higher discharges in summer and lower discharges in winter (Figure S3). The internal nutrient cycling processes played an important role in influencing in-lake nutrient concentrations. Approximately 128 Gg of ON was released from sediment into water columns in Lake Taihu, and the majority of ON released was further mineralized into NH$_4^+$−N. About 0.12 Gg of TP was released into water column from sediment. Strong seasonal patterns in nutrient cycling processes were observed in Lake Taihu, which could impose potentially strong influences on the ecological processes (Figure 4B and Table S2). As an indispensable process for N removal in lakes, the denitrification rate in different seasons ranged from 23.6 to 795 mgN·m^{-3}·day^{-1}, with a peak rate in autumn (155 ± 96.0 mgN·m^{-3}·day^{-1}) and a valley rate in winter (80.9 ± 41.5 mgN·m^{-3}·day^{-1}). This trend was generally consistent with the field-monitored results in Lake Dianchi, China, which had a denitrification rate of 17.5 mgN·m^{-3}·day^{-1} in August but only 6.4 mgN·m^{-3}·day^{-1} in April.[58]

Lake sediment could play a dual role in the nutrient exchange with overlying water, which could have a different impact (e.g., sediment release or adsorption and nutrient exchange rate) depending on seasons. In summer and autumn, sediment could act as a source of TP for overlying water at a release rate of 12.9 mgP·m^{-3}·day^{-1}. In September, TP contribution by sediment could account for 91% of the total discharges into Lake Taihu. However, in spring and winter, lake sediment could act as a sink for TP in overlying water at a rate of 0.1−5.2 mgP·m^{-3}·day^{-1} (Figure 4B). This trend has been confirmed in a field study on the sediment exchange of soluble reactive P in Meiliang Bay, Lake Taihu,[25] which had a much higher P release rate in summer than that in other seasons. A seasonal pattern was also observed in the sediment ON exchange with the overlying water. For most periods, sediment acted as a source of ON; in summer, however, sediment acted as a sink, possibly due to the organic input from decay of phytoplankton.[59] Apart from the seasonal
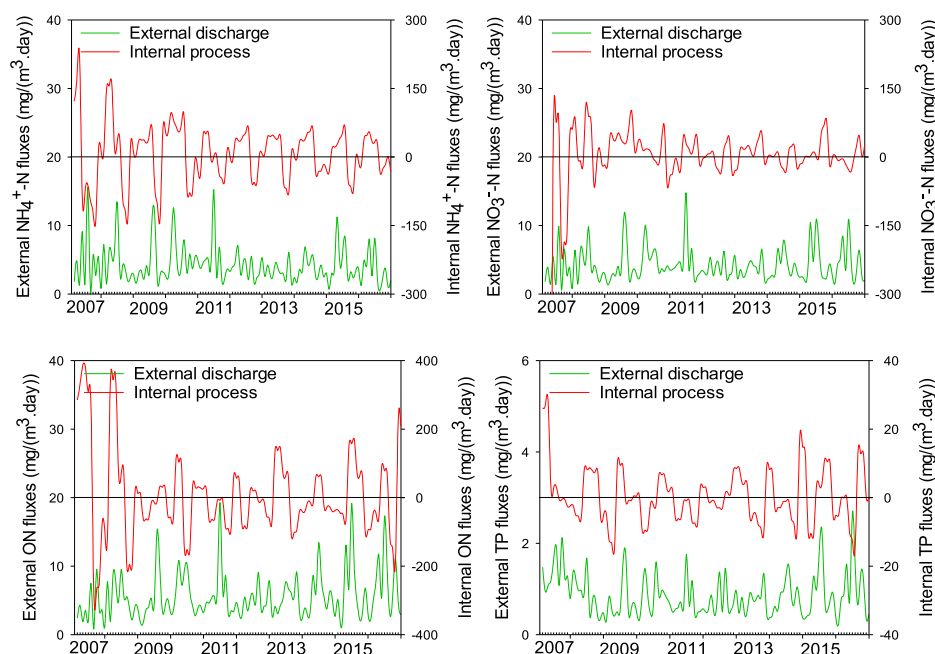
Figure 5. Seasonal changes of external nutrient discharges and internal nutrient loadings in Lake Taihu between 2007 and 2016.
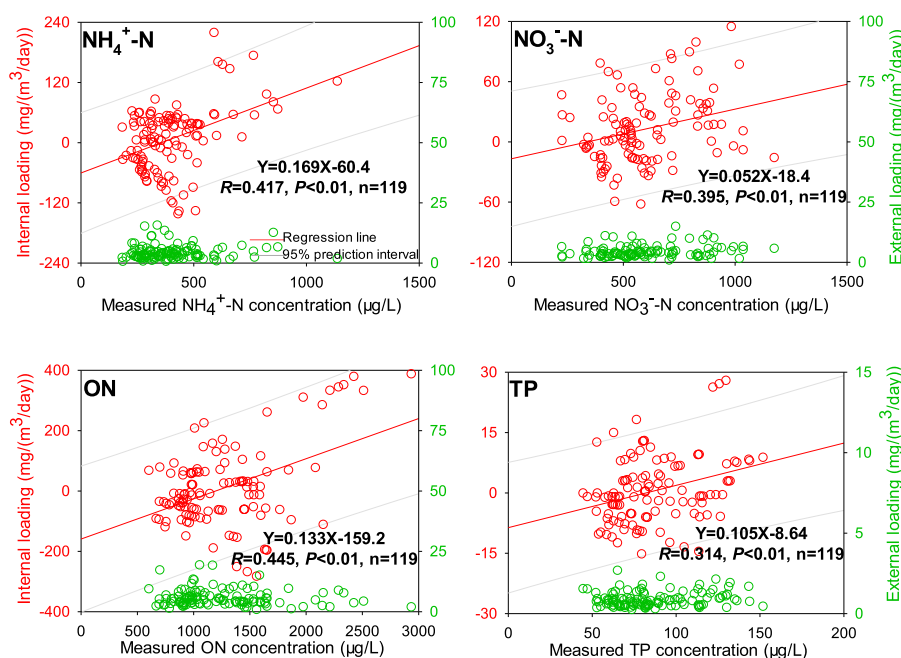

Figure 6. Response of nutrient concentration (NH_4^+-N, NO_3^--N, ON, and TP) to variations of internal nutrient cycling and external discharges.

pattern, yearly variations in external nutrient discharges and internal nutrient cycling were revealed during the study period (Figure S4). For instance, nitrification rate in Lake Taihu was 171 ± 95.1 mgN·m^{-3}·day^{-1} in 2007, whereas it decreased to 64.4 ± 39.8 mgN·m^{-3}·day^{-1} in 2016.

DISCUSSION

Internal Cycling Processes and Seasonal Dynamics of Nutrient Limitation. By combining different internal cycling processes that could potentially influence nutrient concentrations, Figure 5 describes the net changes in loadings for different nutrients in Lake Taihu between 2007 and 2016. Although external nutrient discharge into Lake Taihu was still

at a high level (Figure S1), it was relatively small and fluctuated less between seasons compared with the internal cycling processes. For instance, the external NH_4^+-N discharge into Lake Taihu ranged from 0.6 to 15.6 mgN·m^{-3}·day^{-1} during the study period, whereas the corresponding internal nutrient cycling loadings could fluctuate from -142.3 to 219.2 mgN·m^{-3}·day^{-1}. Figure 6 further demonstrates that large fluctuations in the internal nutrient cycling could largely determine in-lake nutrient concentrations, and positive relationships were observed between internal cycling loadings and measured nutrient concentrations (for NH_4^+-N, $R = 0.42$, $P < 0.01$, $n = 119$; for NO_3^--N, $R = 0.40$, $P < 0.01$, $n = 119$; for ON, $R = 0.45$, $P < 0.01$, $n = 119$; for TP, $R = 0.31$, $P < 0.01$, $n = 119$).
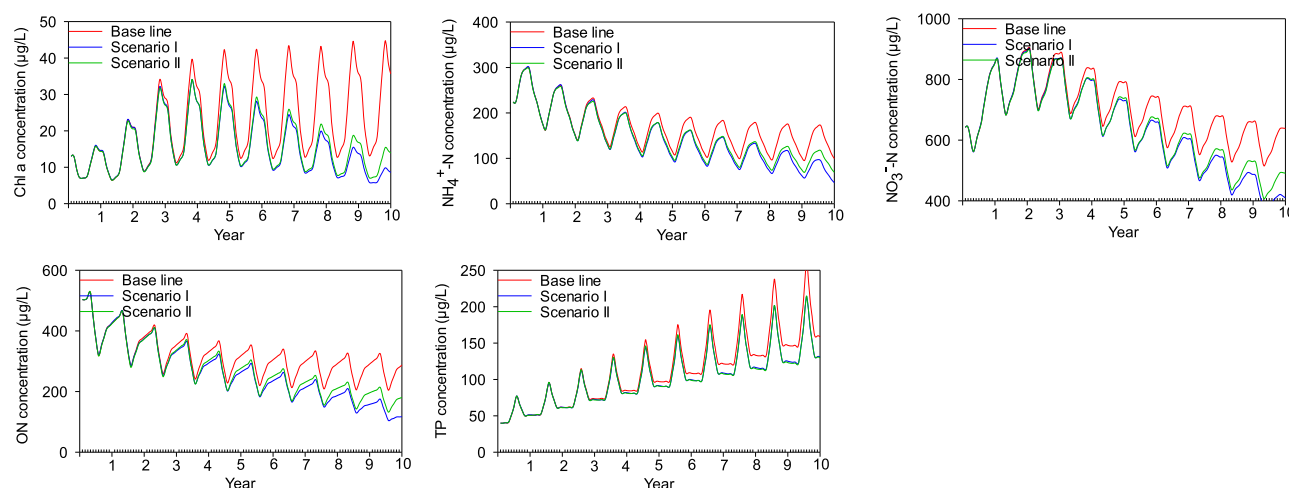
Figure 7. Response of the phytoplankton (Chl *a*) and nutrient concentrations (NH_4^+-N, NO_3^--N, ON, and TP) to different nutrient reduction scenarios. In the baseline scenario, external nutrient discharge in 2016 is introduced as model input and remains stable during a 10 year simulation; In scenarios I and II, a 50% reduction in external N and P discharge compared to that in 2016 is assumed after 10 years. In scenario I, a season-specific nutrient reduction strategy is simulated. In scenario II, reduction of external N and P discharge is achieved without seasonal differences.

Internal N and P cycling processes imposed different degrees of impact, or even opposing impacts, in different seasons on nutrient concentrations in the water column. In summer, intensifying denitrification could result in extremely low NO_3^--N concentrations, while at the same time, the increasing sediment P releases could increase the TP concentrations in water columns. As illustrated in Figure S5, the internal TN fluxes (the sum of NH_4^+-N, NO_3^--N, and ON) were positively correlated with TN/TP ratios in water columns ($R = 0.36$, $P < 0.01$, $n = 119$), whereas the internal TP fluxes were negatively correlated with TN/TP ratios ($R = -0.26$, $P < 0.01$, $n = 119$). Therefore, the asynchronous seasonal dynamics of internal N and P cycling finally result in the seasonal transformation of nutrient limitation, from limitation of P in spring and winter to colimitation of N and P in summer and autumn.

The impact of internal N and P cycling processes on the seasonal pattern of nutrient concentration and limitation has been hypothesized previously, but quantitative evidence regarding these impacts is relatively limited.[20,60] As shown in Figure 6, with an increase of 10 $mgP \cdot m^{-3} \cdot day^{-1}$ in the sediment P release, there could be an increase of 9.8 $\mu g \cdot L^{-1}$ in TP concentration in overlying water; with an increase of 10 $mgN \cdot m^{-3} \cdot day^{-1}$ in denitrification, there could be a decrease of 19.5 $\mu g \cdot L^{-1}$ in NO_3^--N concentration. A variety of factors could influence the internal nutrient dynamics in lakes. Sediment P release into water columns mainly depends on the chemical diffusions induced by the concentration gradient, which is controlled by the temperature, dissolved oxygen (DO), oxidation−reduction potential, and pH.[20,55] In summer, increases in water temperature could stimulate the mineralization mediated by microorganisms, which could liberate organic-bound P and release it into overlying water.[61,62] Decreases in DO could decrease the redox potentials in the sediment−water interface and reduce Fe^{3+} to Fe^{2+}.[63] This process could induce the release of Fe-bound P in sediment.[63] Intensified sediment P releases in summer have been demonstrated by field monitoring in Lake Dongting,[64] Lake Hongze,[65] and Meiliang Bay, Lake Taihu.[56] Regarding N in lakes, denitrification is the utmost important route to remove excessive N.[25] It is a process mediated by anaerobic

microorganisms in the sediment−water interface. Activities of these microorganisms could be significantly affected by water temperature, DO, and organic matter.[66] Lower DO and input of reducible organic substances from decay of phytoplankton could promote the denitrification process in summer.[67] In this study, the estimated denitrification rate in Lake Taihu ranged from 23.6 to 795 $mgN \cdot m^{-3} \cdot day^{-1}$, with 155 $mgN \cdot m^{-3} \cdot day^{-1}$ in autumn and 80.9 $mgN \cdot m^{-3} \cdot day^{-1}$ in winter. These values are generally approaching the reported values in lakes from previous studies (ranging from 42 to 214 $mgN \cdot m^{-3} \cdot day^{-1}$) (Table S3). For instance, in Lake Baldegersee, Switzerland, the annual average denitrification rate was 66.8 $mgN \cdot m^{-3} \cdot day^{-1}$;[63] in Lake Võrtsjärv, Estonia, the annual average denitrification rate was 80.0 $mgN \cdot m^{-3} \cdot day^{-1}$.[68]

Response in Water Quality to Future Reduction of External Discharge. For eutrophic lakes with a long history of nutrient accumulation, internal cycling processes could prevent the quick improvement in water quality and maintain eutrophication in lakes.[16,17] Characteristics in the seasonal pattern of internal nutrient dynamics may require corresponding changes in reduction strategies of external N and P discharges. In Figure 7, we simulated three typical scenarios to examine the effects of nutrient reduction and different reduction strategies to improve water quality in Lake Taihu. The simulated results showed that the growth of phytoplankton could respond only after 4−5 years' continuous external reduction, which is similar to a previous study carried out in Lake Erie, United States.[69] N species in the lake, which could be removed by denitrification, could have quicker responses, whereas TP concentration may experience a continuous increase probably due to the loading from lake sediment. In addition, a season-specific nutrient reduction strategy, which focuses on the external P reduction in summer and autumn, while focusing on the external N reduction in spring and winter, could have 30% more reduction (on an annual basis) in Chl *a* concentration than the season-unspecific strategy over 10 years. More reduction could be observed in the concentrations of N species in water columns (Figure 7).

Implication for Future Lake Eutrophication Control. After years of efforts on reduction of external nutrient discharges, Lake Taihu has transformed from a lake mainly

driven by external discharges a decade ago[20,37] to a lake dominated by internal processes now. This makes nutrient concentrations in water of Lake Taihu respond more actively to the seasonal variations caused by internal processes. Driven by asynchronous dynamics in the internal N and P processes (e.g., increasing sediment P release and intensifying denitrification), a seasonal transformation from P limitation in spring and winter to colimitation of N and P in summer occurred yearly in Lake Taihu. This point was also illustrated by the in situ nutrient enrichment bioassays in Lake Taihu.[20] In spring and winter, the growth rate of phytoplankton increased significantly with P additions.[20] However, in summer and autumn, N additions alone revealed a significant positive effect on the phytoplankton growth, and P additions only stimulated plankton growth once N was added.[20] The seasonal pattern in nutrient limitation has been increasingly emphasized with prevalence of the "N + P control" paradigm in lake eutrophication control.[14,70] To limit the intrinsic growth rates of cyanobacteria blooms in summer, the threshold values for TN and TP concentrations in Lake Taihu were estimated to be below 800 and 50 $\mu g \cdot L^{-1}$,[38] respectively. Driven by intensifying denitrification in summer, the measured TN concentrations in Lake Taihu had already approached the estimated threshold values in summer (869 ± 158 $\mu g \cdot L^{-1}$ in September), whereas the monitored TP concentration ($71-130$ $\mu g \cdot L^{-1}$ in summer and autumn) was much higher than the threshold values due to the intensifying sediment release. Thus, different internal processes in Lake Taihu could cause different amplitudes or even opposite directions on seasonal fluctuations in nutrient concentrations.

A more clear understanding about the relationships between the growth of phytoplankton and internal nutrient cycling will be helpful for water quality improvement in the future. The strong seasonal patterns in both nutrient concentration and N/P ratios in Lake Taihu could potentially influence the growth of phytoplankton, their community composition, and their toxin production.[71,72,73] Based on Liebig's law of the minimum, N or P limitation is regarded as the key factor for determining the growth of phytoplankton in lakes.[74] Because of the ability to fix N_2 from atmosphere, many bloom-forming species of cyanobacteria could dominate at lower water N/P ratios.[75] This fact was demonstrated in an analysis of phytoplankton growing season data from 17 lakes worldwide.[76] In contrast, the elevated water N/P ratios could favor some algal species with stronger competitive abilities for using P[21] and affect the per-cell production of toxins by such cyanobacteria.[10] In a recent study, an increase in the dominance of cyanobacteria (mainly *Microcystis* spp.) in summer and autumn in Lake Taihu was mainly attributed to the changes in water P concentrations.[77] Similar scenarios have also been documented in diverse lakes, such as Lake Zurich in Switzerland,[78] Lake Okeechobee, United States,[79] and Lake Erie in the United States−Canada.[80] Besides, the growth of phytoplankton and their community compositions could also be influenced by the relative compositions of different N species.[57] High $NO_3^- -N$ concentration in the water could favor the growth of eukaryotic phytoplankton,[57] whereas low $NO_3^- -N$ concentration concurrent with sufficient $NH_4^+ -N$ could favor some cyanobacteria species.[81] Non-N_2-fixing phytoplankton species prefer $NH_4^+ -N$ over $NO_3^- -N$ and would be outcompeted by other species under high-$NO_3^- -N$ conditions due to a low assimilation rate.[82]

It should be noted that in this study, we treated Lake Taihu as a whole without addressing spatial variances in lake. The growth of phytoplankton, which is dominant in the majority areas of Lake Taihu, is addressed in the present model. However, in fact, in the east of Lake Taihu, there are still some areas of macrophytes distributed at the shores or in the bays.[49,50] This suggests that our modeling results may well simulate temporal variations of nutrient concentration and internal cycling processes in the majority areas of Lake Taihu but may be not applicable for the areas where macrophytes are still distributed.

In summary, water management strategy in restoration of eutrophic lake should be reconsidered and updated in time with the change in the relative importance of external discharge and internal nutrient loading. For Lake Taihu, as nutrient dynamics are mainly driven by internal processes now, it is more and more important to reduce internal loadings to improve water quality within a short time. The possible engineering measures could include sediment capping, sediment dredging, and encouraging macrophyte growth in some typical areas (e.g., Meiliang Bay).[5] However, the control of external nutrient discharge should not be thus loosened, since flux is still at a high level now, and it will feed internal loading on the long term. More efforts are needed to clearly understand the potential impacts caused by internal cycling processes on the growth of phytoplankton and shifts in their community composition in Lake Taihu, since they are closely related to the functioning of the entire food web.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.9b04266.

> Monthly total discharges of ammonia ($NH4^+ -N$), nitrate ($NO3^- -N$), organic nitrogen (ON), total nitrogen (TN), and total phosphorus (TP) into Lake Taihu during the study period (Figure S1); monthly variation of chlorophyll a (Chl a), ammonia ($NH^{4+} -N$), nitrate ($NO3^- -N$), organic nitrogen (ON), total phosphorus (TP), and nutrient ratios (TN/TP, TN/$NH^{4+} -N$, TN/$NO3^- -N$, and TN/ON) in Lake Taihu (Figure S2); external discharges of ammonia ($NH^{4+} -N$), nitrate ($NO3^- -N$), organic nitrogen (ON), and total phosphorus (TP) (Figure S3); yearly changes in external nutrient discharges and internal nutrient cycling (Figure S4); response of the TN/TP ratio to the variations of internal TN and TP loadings (Figure S5); definitions and values of the selected parameters in the models (Table S1); results of the hierarchical parameters in the model (Table S2); denitrification rates of lakes in previous studies (Table S3) (PDF)

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