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Human Activities Altered Water N:P Ratios in the Populated Regions of China

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Abstract

Being able to quantify nutrient stoichiometry in the waterbodies is especially important given its strong effects on a variety of ecological processes. China has made huge progress in the improvement of surface water quality, but the accompanying changes to water nutrient stoichiometry and implications are not well understood yet. Our results have shown that the water nutrient cycles have been decoupled in China's populated regions, and population density and GDP values in the belonging catchment are useful in explaining the variances of lake N:P stoichiometry in East China Lake Region. In other regions, water N and P tend to respond to the selected parameters in a similar way, leading to the poor prediction of N:P stoichiometry. With the progress of water management in China, a similar change of water nutrients and their stoichiometry as the developed countries is occurring, i.e., faster decrease of TP concentrations than TN, and continuing increase of N:P ratios. It is necessary for the managers to be aware of the quick and large-scale changes of nutrient stoichiometry in the water, since the ecological risk caused by the changes to the aquatic systems is still not well known. .

Keywords

Decoupled nutrient cycle; nutrient stoichiometry; eutrophication; human activity; water management progress

1. Introduction

Human-induced nutrient flow (e.g., nitrogen (N) and phosphorus (P)) has become an important part of the biogeochemical nutrient cycles in the surface-earth systems (Elser and Bennett, 2011; MacDonald et al., 2011; Peñuelas et al., 2012; Bouwman et al., 2013; Peñuelas et al., 2013; Tong et al., 2015). In the recent decades, the cycling pattern has been largely altered due to the intensified human activities (Peñuelas et al., 2012, 2013), bringing more N and P loadings to the biospheres than the pre-industrial periods (Smil, 2000; Bennett et al., 2001). Massive fertilization driven by increasing demand for food has caused intensified utilization of synthesized fertilizer of N and P. Main form of N utilized is ammonia created by Haber-Bosch reaction (Erisman et al., 2008), while the P-containing fertilizers mainly come from the P-containing minerals (Cordell et al., 2009; Cordell and White, 2014). Due to the tendency of overusing fertilizers to guarantee the crop yield, excess N and P loadings from the fertilization are entering into aquatic environment as well as various other human sources, such as sewages discharges and animal dung (Elser and Bennett, 2011; Peñuelas et al., 2012; Cui et al., 2013; Morée et al., 2013; Tong et al., 2017a), resulting in the eutrophication and subsequent degradation of water quality and loss of aquatic biodiversity (Correll, 1998; Carpenter, 2008; Conley et al., 2009; Le et al., 2010; Stone, 2011). Currently, the control of water eutrophication has become the priority in China's water pollution controls. China has a total of 2,693 lakes (with an area >1 km^2) and 8.2×10^4 km^2 in total areas (Wang and Dou, 1998; NIGL, 2015). Lakes among different regions could vary significantly in the water volume, lake depth and water residence time (Wang and Dou, 1998; NIGL, 2015). The majorities of China's lakes are rather shallow, and have been eutrophicated or are being eutrophicated (Le et al., 2010; Huang et al., 2014). For example, in the Taihu Lake, the most damaging and extensive outbreak of harmful algal blooms (HABs) occurred in 2007, which severely affected the water supplies in Wuxi City (a shore city near the Taihu Lake) and left over two million people without drinking waters for several weeks (Stone, 2011). Other Chinese lakes are also experiencing similar situations (Le et al., 2010; Liu et al., 2016).

There has been a prolonged debate about the key factors and detailed mechanisms that dominate the lake eutrophication and HABs' occurrences (i.e., "P-only" paradigm or “P + N” paradigm) (Carpenter, 2008; Paerl et al., 2011, 2016; Schindler et al., 2016). The general consensus is that, regardless of aquatic system types (i.e., marine or freshwater systems), limitation of algal growth in the water is a combination of water N and P concentrations, and water N:P ratio as well, rather than by P or N alone (James et al., 1994; Cotner, 2016; Guildford and Hecky, 2000; Paerl et al., 2011, 2016). Hence, the accurate understanding about the coupling of N and P concentrations in the waterbodies is the first step to take the correct strategy to curb water eutrophication. P in the water is traditionally considered as the limiting nutrient of algal growth based on the long-term lakes’ experimental manipulations studies, because N can be obtained by plants through ubiquitous atmospheric deposition and biological fixation (Bergström et al., 2005; Elser et al., 2009). However, the prevailing P limitation in the freshwater ecosystems could also be altered due to the intensified P inputs from human activities (Schindler, 1977; Elser et al., 2007). N and P loadings to aquatic systems largely depend on the external nutrient input besides the internal loading and natural weathering, and the source compositions are determined by the stage of industrial and agricultural development, and strategies of water management (Downing and Mccauley, 1992; Carpenter, 1998; Arbuckle, 2001; Yan et al., 2016). Since 2005, in China, many strategies on the industrial and domestic sewage control, and large investment in the environmental reforestation have caused the significant reduction of external nutrient loadings to the aquatic systems (Tong et al., 2017b; Zhou et al., 2017), but the accompanying changes on lake nutrient stoichiometry and implications to the water management strategies are not understood yet.

Nutrient loadings in the aquatic systems are largely affected by a number of factors, such as land use types, economic development, sanitation facility, and hydrology conditions in the catchment (Kellerman et al., 2014; Kothawala et al., 2014). Many studies have been undertaken to elucidate the relationship between nutrient concentrations and land use types in the catchment (Müller et al., 1998; Maberly et al., 2003; Carney, 2009; Liu et al., 2011; Kothawala et al., 2014). However, the obtained information from the existing land use types based on the remote sensing data is still insufficient (Collins et al., 2017). Population density and industrial development stages in the catchments are also important factors which could reflect the changes of water nutrient status (Duan et al., 2009; Yan et al., 2016). Hence, the response of water nutrients to human activities in the catchment is a combination of various drivers, rather than to a single driver or factor, and this fact has also increased the difficulty in identifying the specific driving forces to lake nutrients in the catchment (Collins et al., 2017).

Being able to quantify nutrient stoichiometry is especially important given its strong effects on a variety of ecological processes, i.e., primary production (Conley et al., 2009; Paerl et al., 2016) and food webs (Elser et al., 2010) in aquatic systems. Accurate understanding of the relationship between various human activities, and water nutrient concentrations and their stoichiometry in the catchment is crucial to make the targeted strategies to cope with the water eutrophication problem. In this study, based on the paired N and P monitoring data from 800 lakes or reservoirs in 2014, we have explored the statistical correlations between major variables and corresponding water nutrients in the belonging catchment to explore the key drivers responsible for the variations of water nutrients and their stoichiometry. We have also compared the changes of water nutrient concentrations and their stoichiometry during different historical periods in China (from the year of 1988 and 1992, and from the year of 1995 to 2005, and 2014, respectively) to identify the potential impacts from water management progress on lake nutrients. China has recently started to reform its water governance structure from administrative divisions to watershed divisions. Based on the characteristics of nutrient stoichiometry and the underlining drivers in the catchments, specific water nutrient management strategies should also be developed in the future.

2. Methods and materials

2.1 Study lakes

China has five typical lake regions in different geographical regions (shown in Figure 1). This division is firstly raised by Sumin Wang and Hongshen Dou in the 1990s (Wang and Dou, 1998), and could better reflect the impacts of surrounding hydrological characteristics, human activities and climate conditions to waterbodies in the catchment (Ministry of Environmental Protection, China, 2013). In details, the five lake region includes the Northeast China Lake Region, Qinghai-Tibet Lake Region, Yunnan-Guizhou Lake Region, Inner Mongolia-Xinjiang Lake Region and East China Lake Region, respectively (shown in Figure 1). Lakes located in different lake regions could vary significantly in the water volume, lake depth and hydrological conditions, respectively (shown in Table S1) (Wang and Dou, 1998). Most of the population and developed industries are located in the East China Lake Region, which is on the east side of China’s geographical boundary “Hu Huanyong Line” (as shown in Figure 1). The “Hu Huanyong Line” is an imaginary line diagonally across China that divides the area of China into two roughly equal parts in total area, the east part of the line contains 94% of the population while the west part of the line contain the rest 6% of the population. In this region, most lakes are fluvial lakes, which are quite shallow and have intensive pollutant loadings from human activities (Table S1). In the East China Lake Region, the widely constructed dams between rivers and fluvial lakes in recent years have also cut the natural water exchanges, which prolonged the water residence time and increased the eutrophication risks. Qinghai-Tibet Lake Region has the largest number of lakes, and these lakes are mostly located in the regions with sparse population and few industries. In Inner Mongolia-Xinjiang Lake Region where it is mostly arid and semi-arid climate, lakes are shrinking at an increasing pace due to the limited water supply and strong evaporation (Tao et al., 2015). At the same time, industries and intensive agriculture activities are also competing for the limited water resources in this region (Ministry of Environmental Protection, China, 2013).

In this study, all of the water quality data are a part of the randomized, unequally weighted probability surveys overseen by Ministry of Environmental Protection, China, with the goal to create the unbiased assessments of water quality in the freshwater lakes across different provinces in China (Tong et al., 2017b, c; Zhou et al., 2017). In details, we have followed three main guidelines during the selections of waterbodies: 1) with long-term and continuous nutrient monitoring data in 2014. Only the lake or reservoirs with over 10 monthly TN and TP monitoring data have been selected. 2) with significant variances in the hydrological characteristics and climate conditions. To make the results representative, we have selected the lakes or reservoirs with different hydrological characteristics (e.g., lake depth, surface area and water volume) and climate conditions (e.g., temperature and precipitation). 3) with different levels of interferences from the human activities. We have tried to select the lakes or reservoirs in different regions to cover various types of human activities (e.g., farming area, developed region and less-developed region).

2.2 Water nutrient data

The paired N, P monitoring data and their stoichiometry from 800 lake or reservoir sampling sites in 2014, distributed in China's five lake regions, have been collected and analysed as a response to various drivers in the watersheds. The nutrient monitoring in each sampling site was carried out monthly in 2014, and the annual average concentration was calculated to represent the general nutrient conditions of waterbodies. The standard of sampling site selection and procedure of water collections are consistent based on the “Technical Specifications Requirements for Monitoring of Surface Water and Waste Water in China”. An unfiltered aliquot of the surface water is prepared from each bulk sample. Measurement of TN concentration is based on continuous flow analysis and N-(1-naphthyl) ethylene diamine dihydrochloride spectrophotometry (Ministry of Environmental Protection, China, 2013), with the detection limit of 40 μg/L (Tong et al., 2017c). TP concentration is determined by persulfate digestion, followed by automated colorimetric analysis by using a flow injection analyzer, with a method detection limit (MDL) of 5 μg/L (Tong et al., 2017b).

2.3 Potential driving variables for water nutrients

In the analysis between water nutrients and human activities in the catchment, the five lake regions are further divided into 81 catchments (as shown in Figure S1). Water nutrient concentrations and their stoichiometry were used to be correlated with the corresponding driving variables in the catchment. The variables in driving the changes of lake nutrients and their stoichiometry considered in this study are provided in Table 1. These variables could generally reflect the impacts of human activities and industrial development, nutrient inputs from the terrestrial sources, nutrient inputs from atmospheric sources and nutrient transport on the lands. In details, we have selected the land use and land cover (LULC), regional population density, economic development level (evaluated as Gross Domestic Product (GDP) value), nutrient productions from livestock’s manure, atmospheric N depositions, annual precipitation and land soil erosions in the catchment to identify the potential impacts to water nutrients and stoichiometry. Population density and local GDP values in China are extracted for the individual catchment by using ArcGIS 10.1 software (data available at: Data Center for Resources and Environmental Sciences, Chinese Academy of Sciences, http://www.resdc.cn). LULC compositions of 81 individual catchment are extracted from the country-wide land cover data, interpreted from the Landsat TM images (data available at http://www.resdc.cn/). Seven typical land use types are classified in the existing LULC map, which are crop land, forest, grassland, water bodies, cities, bare soil and sea reclamation, respectively. Nutrient productions (including N and P, respectively) from livestock's manure in China are extracted from a global-wide manure's nutrient production dataset (West et al., 2014). The livestock considered in the manure's productions included cattle, buffalo, goat, sheep, pig and poultry, respectively (West et al., 2014). Atmospheric N deposition rates in the catchments were extracted from the global dataset of atmospheric N depositions (Peñuelas et al., 2013). Considering the significant impacts of precipitation to nutrient's transport in the lands, annual precipitation data was also extracted for different catchments (data available at http://www.resdc.cn/). The percentage of land soil's area with the moderate and severe erosions in the catchments was extracted from the China's national land soil erosions' map (data available at http://www.resdc.cn/).

2.4 Data analysis

To understand the driving forces for the changes of water nutrients, we have first performed the correlation analysis to indicate the strength of the relationship between each type of various human activities and lake or reservoir N, P concentration and N:P ratio in the catchment. Then, we have conducted a multiple general linear model (GLM) analysis to quantify the relative contributions of each type of human activities to changes in water N, P concentrations and their stoichiometry in the catchment. In the GLM analysis, a stepwise method is applied to reduce the model selection biases, based on the information-theoretic approach and Akaike information criterions (Burnham and Anderson, 2002). In this study, the statistical analyses were conducted by the Excel 2010 (Microsoft, USA), SPSS 16 (SPSS, USA), and R software.

3. Results

3.1 Water nutrients and their stoichiometry

Figure 2 provides the TN concentrations (Figure 2A), the TP concentrations (Figure 2B) and the corresponding TN:TP mass ratios (Figure 2C) in the selected lakes or reservoirs in 2014. The statistical results and frequency distributions of TN concentrations, TP concentrations and TN:TP mass ratios in the waterbodies are shown in Table 2 and Figure S2. The highest lake TN concentrations (910(320.8-4001.3) μg/L) (median and 95% confidence interval) was observed in the East China Lake Region, while the lowest TN concentrations (690(292-2050) (median and 95%CI) μg/L) occurred in the Northeast China Lake Region. The highest TP concentration was observed in the Northeast China Lake Region (41(22.7-100.0) (median and 95%CI), μg/L), while the lowest TP concentrations (26(6.6-153.7) (median and 95%CI), μg/L) occurred in the Yunnan-Guizhou Lake Region (Table 2). Most of the water TP concentrations are lower than 50 μg/L (Figure 1B and Table 2), which is Grade III limit based on China's surface water quality standard (based on GB 3838-2002) (Ministry of Environmental Protection, China, 2002). Regarding to the spatial distributions, higher water TP concentrations (>50 μg/L) are usually observed in the waterbodies located in the middle Yangtze River Basin of East China Lake Region (Figure 2B), while the lower TP concentrations generally occur in the Qinghai-Tibet Lake Region and south of East China Lake Region (Figure 2B). Unlike the TP concentrations, the higher lakes' TN concentrations are usually observed in the northern part of East China Lake Region (Figure 2A). Generally, the reported TN and TP concentrations (Figure 2A and 2B) are higher than the good lake's TN and TP limits, which is usually adopted by the European countries (i.e., ~500 μg/L for TN and ~25 μg/L for TP, respectively) (Phillips and Pitt, 2015), UK water quality standard (i.e., 1500 μg/L for TN and 20 μg/L for TP, respectively, Table 2) and Norway water quality standard (i.e., 600 μg/L for TN and 20 μg/L for TP, respectively, Table 2). In all selected lake regions, the water TN concentrations and TP concentrations ($\log_{10}$ transformed) are strongly and positively correlated (with $P<0.01$ in all the selected lake regions, Figure 3).

Figure 2C shows the TN:TP mass ratios in all the sampling sites in 2014. The lowest TN:TP mass ratio is 16.8(8.0-31.3) (median and 95%CI, unitless) in the Northeast China Lake Region, which is much lower than the corresponding values from the other lake regions (24.4(6.9-170.7) in the East China Lake Region, 23(5-161.7) in the Inner Mongolia-Xinjiang Lake Region and 28.9(5.5-151.2) in the Yunnan-Guizhou Lake Region, respectively) (Table 2). In the fresh waters, N limitation of algal growth is assumed to occur at water TN:TP mass ratios <9, while P limitation of algal growth in the waterbodies can occur when the mass ratio is >23 (Guildford and Hecky, 2000). In our study, 78 in a total of 800 lakes has TN:TP mass ratios lower than 9 (mostly in Northeast China Lake Region), while over 50% of all the sampling sites (a total of 417 sites) has the TN:TP mass ratios higher than 23 (Figure 2C, mostly in the East China Lake Region). This result indicates that, in China, only a small percentage of the waterbodies could be N limited, while the majority could be P limited for the algal growth in aquatic systems.

3.2 Potential driving variables for water nutrients

Figure S3 provides the major drivers in the catchment that could impose potential impacts on water nutrients and their stoichiometry. Among different catchments, the main land use types could vary significantly (Figure S3A). The agricultural croplands and forests usually dominate the land use types in the East China Lake Region (39.2(15.3-76.7)%) and Northeast China Lake Region (35.8(11.8-74.0)%) (Figure S3A). Urbanization has covered a high proportion of land areas in the East China Lake Region (8.0(1.3-22.6)%), especially in the downstream of China's major river basins, i.e., downstream of Yangtze River Basin and Pearl River Basin (Figure S3A). Higher population density (Figure S3B) and higher GDP values (Figure S3C) in the catchment are also observed on the east side of China's population distribution boundary "Hu Huanyong Line" (as shown in Figure 1), i.e., East China Lake Region, part of Yunnan-Guizhou Lake Region, and Northeast China Lake Region. The regions with low population density and low GDP values usually occurred in the Qinghai-Tibet Lake Region and Inner Mongolia-Xinjiang Lake Region (Figure S3B and S3C). Population density and GDP values could vary significantly among the catchments, with a range of 0.18-1539 capita/km^2 in population density and a range of 0.36×10^4-6355×10^4 RMB/km^2 in GDP values, respectively. For the N and P productions from the livestock's manure, hot spots were usually observed in the East China Lake Region, Yunnan-Guizhou Lake Region and some regions of the Qinghai-Tibet Lake Region (Figure S3D and S3E). Atmospheric nutrient deposition has been reported to cause a significant change in waterbodies' nutrient compositions, especially in the relatively undisturbed regions (Elser et al., 2009; Liu et al., 2013). From the country level, higher atmospheric N deposition rates were observed in the East China Lake Region (Figure S3F), and low deposition rates were observed in the other regions. Precipitation in the catchments has both dilution and erosion effects on the nutrients from soils to lakes. Figure S3G shows that the higher annual precipitation usually occurs in the south of East China Lake Region and Yunnan-Guizhou Lake Region, where the highest annual precipitation could be over 5000 mm per year. The regions with the severe soil erosions were generally located in the Inner Mongolia-Xinjiang Lake Region and Qinghai-Tibet Lake Region (Figure S3H).

3.3 Decoupled water nutrient cycles in the populated regions

Water nutrients are related to different environmental drivers in different ways, and N and P may or may not be related to the driver in a similar way (Collins et al., 2017). Similar relationships for both nutrients would lead to a parallel response, leading to the weak prediction of nutrient stoichiometry, while different relationships for each nutrient would cause a single response, leading to a strong prediction of stoichiometry (Collins et al., 2017) (as illustrated in Figure S4). Population density, cropland area and economic development stages in the catchment are important indicators to reflect potential impacts from human's domestic discharges, agricultural activities and industrial development to waterbodies (Peñuelas et al., 2013; Yan et al., 2016; Collins et al., 2017). Figure 4 shows the correlations between population density, cropland area and GDP values in the catchment, and water TN:TP mass ratios. In general, cropland area in the catchment is not a proper predictor of water N:P stoichiometry. Population density and GDP value only work for the East China Lake Region. In the East China Lake Region, a positive relationship was observed between population density in the catchment and TN:TP mass ratios ($\log_{10}$ transformed, R=0.43, P=0.00, n=531). However, in the other lake regions, the corresponding relationship was not significant (P>0.1, Figure 4A). As indicated from Figure 4B, the correlation between cropland area in the catchment and nutrient stoichiometry is not significant in all the selected lake regions (P>0.05). Similar to the population density, the economic development levels in the catchment could also have a positive impact to water TN:TP ratios in the East China Lake Region (R=0.521, P=0.00, n=561), but these impacts in other lake regions are not significant (Figure 4C). The results strongly indicated that in most regions of China (i.e., Yunnan-Guizhou Lake Region, Northeast China Lake Region and Inner Mongolia-Xinjiang Lake Region), water N and P have a similar response, and it is therefore difficult to have a good indicator of the N:P stoichiometry. However, excessive human activities in the densely populated and economically developed East China Lake Region decoupled the linkage of N and P response causing human related factors to be a good predictor of N:P stoichiometry. Higher TN:TP mass ratios in the waterbodies tend to occur in the populated and developed regions of China, which might be possibly attributed to the unbalanced removal of N and P from the sewages in the developed regions (Atwm and Langeveld, 2017). A large-scale monitoring of the USA's lakes also proved the decoupling of N and P response due to human activities where higher lakes' TN:TP mass ratios occurred in the more impacted Midwestern Region than the less disturbed Northeastern region (Collins et al., 2017).

4. Discussions

4.1 Importance of various predictors on the nutrient stoichiometry

Table 3 provides the correlations between population density, cropland areas and GDP values in the catchment and water nutrient concentrations (TN and TP, respectively) in different lake regions. In the East China Lake Region, water TP concentrations have significant negative correlations to the population density and GDP levels in the catchment, the TN concentrations also show negative correlation to these two variables though it is not significant (Table 3). The more developed areas in

China (higher GDP per capita) represent more stringent environmental standards. This can be reflected by the fact that provinces in East China Lake Regions usually have higher percentage of the centralized urban wastewater treatment facilities, higher percentage of rural sanitation facilities (Tong et al., 2017b, c), and the most developed Beijing-Tianjin-Hebei Region, Yangze River Delta and Pearl River Delta regions all have higher wastewater discharge standards than the rest regions of China (Tong et al., 2017b, c; Zhou et al., 2017). This indicates that East China provinces have transformed its traditional way of economic development and are less willing to sacrifice environment for fast economic development. This single response leads to the strong prediction of water TN:TP mass ratios. However, both TN and TP concentrations in the waterbodies responded strongly to the cropland area percentage in the catchment, leading to the weak response of water TN:TP mass ratios to the cropland area. In the Yunnan-Guizhou Lake Region, population density, GDP values and cropland area have significant impacts to water TN and TP concentrations (Table 3).

Besides the population density, economic development and crop land area in the catchment, there are some other variables that could potentially affect the water nutrients and their stoichiometry. Table 4 has summarized the correlations between the other driving variables and water nutrients in the catchment. In the East China Lake Region, the livestock's manure N:P mass ratio, atmospheric N deposition and annual precipitation in the watersheds are also possible predictors of water TN:TP mass ratios (with $P<0.01$, shown in Table 4), although the correlation is weaker. The impacts of atmospheric N depositions to water nutrient stoichiometry have been demonstrated in previous studies. Elser et al. (2009) has reported that the atmospheric N deposition could shift the N:P stoichiometry in the lakes of Norway, Sweden and United States, significantly. The lakes in regions with higher atmospheric N depositions could have a TN:TP ratio three times as high as the lakes in regions with the low N deposition (Elser et al., 2009). The forest region, urban construction area and soil erosion area in the watersheds have strong correlations with both of the water TN and TP concentrations, respectively (Table 4, with P<0.01), further leading to the parallel response in predicting their stoichiometry. In the Yunnan-Guizhou Lake Region, there are some variables which could effectively reflect the impacts to the water TN and TP concentrations, but these variables are not effective in decoupling the TN and TP concentrations (Table 4).

GLM analysis is also conducted in order to quantify the contributions of different variables to explain the variations of water TN concentrations, TP concentrations and TN:TP ratios in the catchment (Table 5). The results showed that in the East China Lake Region, the selected variables could explain 38%, 37% and 38% of variations of water TP concentrations, TN concentrations and N:P mass ratios, respectively (Table 5). However, the selected variables failed to explain the water nutrient variations in other lake regions, with a total explained variance less than 5%. For the water TP variations in East China Lake Region, GDP values in the catchment could explain 46% of the total explained variances, while the TN concentrations could be mostly explained by the nutrient transport process, including precipitation (explaining 38% of the total variances) and land soil erosions (explaining 21% of the total variances) in the catchment. For the water TN:TP mass ratios, precipitation, land soil erosions, local GDP values, and N:P production ratios from livestock's manure in the catchment could be the dominant factors in explaining the variations (Table 5), and each driver could explain over 10% of the total variances in water TN:TP ratios (precipitation (25.8%), soil erosions (23.0%), GDP values (20.7%), livestock's manure N:P ratio

(10.8%), respectively).

Nutrient stoichiometry in the freshwater systems could be highly variable compared with the other aquatic systems (i.e., ocean and sea), due to its stronger connections to various driving variables (Duan et al., 2009; Meter and Basu, 2015). Some human activities could possibly decouple the N and P accumulations in the lakes, and could be applied to predict the lake nutrient stoichiometry in the populated and developed regions. This point has also been confirmed in the nation-wide scale survey about lake N:P stoichiometry in the undisturbed and heavily impacted regions of the USA (Collins et al., 2017). The studies from Iowa, USA, have also demonstrated that the lakes' N:P stoichiometry could be explained by the land use types, because N is associated with row crop agriculture while P could be more associated with pasture agriculture (Arbuckle and Downing, 2001). Legacy of soil nutrients have been suggested to be important nutrient sources for aquatic systems in the agricultural regions (Jarvie et al., 2013; Meter and Basu, 2015; Powers et al., 2016). TN:TP mass ratios in the land soils are usually lower than the corresponding values in the waterbodies. However, N in the soils is more mobile than P, while P in the soils, mainly in the particulate forms is usually mobilized with soil particles under heavy rainfall (Peñuelas et al., 2013). The particulate P in the lakes could also accumulate more easily in the lake sediment (Shinohara et al., 2016).

4.2 Evolution of China's water nutrient stoichiometry with management progress

Water management and pollutant control measures could affect nutrient concentrations and their stoichiometry in the lakes significantly (Cui et al., 2013; Liu et al., 2016), because some water pollution control strategies might be effective in removing one nutrient from sewages, but may be not effective in removing the others (Atwm and Langeveld, 2017). As a comparison, we have also collected the nation-wide lake or reservoir nutrient monitoring concentrations enduring from 1988 to 1990 and from 1995 to 2005, respectively, which could reflect the changes of waterbodies' nutrients accompanying with the progress of China's water management. During the 1988-1990, few strategies on water pollution controls have been made in China, and water environment protection is largely ignored in the governmental development policy making. However, during this period, China's industry in some regions has started to develop after the "Reform and Opening-up". During the 1995-2005, China's industry and economics developed quite fast. The importance of environmental protection started to emerge, and several policies on water pollution control have been issued. After decades of development, in 2014, industrialization and high GDP values have already been achieved in many eastern regions of China. Currently, the major polices for alleviation of water pollution in China are national wastewater discharge standards and pollutant cap-control targets, revised every five years through the National Five-Year-Plan. Many water laws, guidelines, and regulations on the water pollution controls have been issued and revised between 2005 and 2014 (Tong et al., 2017b). As the most important strategies on water pollution control, these efforts in the China's water management progress could be reflected in the rapidly increasing accesses to wastewater treatment plants (WWTPs) in the urban and improved toilets in the rural areas (Tong et al., 2017b, c). Figure 5 provides the changes of nation-wide water TN concentrations, TP concentrations and TN:TP mass ratios during these three periods, respectively. Compared with the period of 1988-1990, TN concentrations in the lakes have slightly increased to 1533(314-7347)μg/L (median and 95% CI) during the 1995-2005, while the corresponding water TP concentrations have increased to 86(11-602)(median and 95% CI) μg/L. However, a rapid decrease in water nutrient concentrations has occurred in

China after 2005. In 2014, the waterbodies' TN and TP concentrations have decreased to 868(279-3690)(median and 95% CI) and 30(7.35-208) (median and 95% CI) μg/L, respectively. Water TN concentrations and TP concentrations have decreased by a percentage of ~43% and ~65% during the past decade, respectively, and the decrease rate of TP concentrations was much higher than that of TN. On the contrast to the decrease of water TN and TP concentrations, we also find that the water' TN:TP ratios have continuously increased during the past three decades, which were 13.6(2.0-52.3) during 1988-1990, 18.2(4.8-68.6) during 1995-2005, and 23.9(6.2-160.7) in 2014, respectively (Figure 5). The continuing increase of nutrient stoichiometry might bring adverse ecological problems to aquatic systems. Producer diversity in aquatic systems is likely to be affected when resource supply ratios are skewed in favor of one particular nutrient relative to others (Elser et al., 2009). The increasing N:P mass ratios in the lakes might be even worse for further water eutrophication control (Glibert et al., 2014), because it could further favor the occurrences of HABs due to the adaptive physiology of many HABs to thrive in environments where there is excess N relative to classic nutrient stoichiometric proportions (Elser et al., 2007; Glibert et al., 2014), and increasing toxin of many HABs were also associated with the elevated N:P availability in the water (Glibert et al., 2014).

The easier removal of TP and increase of TN:TP mass ratios in the lakes with the progress of water management in China is not unique, and this point could also be demonstrated in the experience of water management progress in developed countries. Due to the effective collection and treatment of domestic and industrial sewages, excess nutrient loadings from the point source have been curtailed largely after the issue of Clean Water Act (CWA), Water Framework Directive (WFD), European Urban Wastewater Treatment Directive, and other similar laws (Guildford and Hecky, 2000; Bennett et al., 2001; Bergström et al., 2005). Pollutants originating from the diffuse and intermittent sources that are difficult to identify are receiving more attentions and becoming the focus of further water pollution controls (Schindler, 1977; Bennett et al., 2001; Elser et al., 2007, 2009; Cotner, 2016). With the implementation of strict water policies, in the European countries and USA, many freshwater ecosystems have undergone steep declines in TP concentrations (Jeppesen et al., 2005; Van et al., 2009; Potter et al., 2010; Morée et al., 2013). However, N concentrations in freshwater ecosystems may still remain constant despite reducing N loadings due to the diffuse nature of nitrogenous sources, the storage capacity of nitrate in the aquifers and the decreased denitrification induced by water P availability (Sutton et al., 2011; Finlay et al., 2013). Yan et al. (2016) have previously compared the difference of water nutrients before and after 1990 from a large scale monitoring dataset in the Euro-American regions. The reported Euro-American water TN concentrations are 1.08 and 0.77 mg/L before and after 1990, respectively, while the corresponding lake TP concentrations are 0.054 and 0.035 mg/L. However, contrasting to the decrease in TN and TP concentrations in the waterbodies, TN:TP mass ratios have increased significantly from 19.1 before 1990 to 24.7 after 1990.

5. Conclusions

This study revealed the phenomenon of decoupled N and P responses due to the intensified human activities in China. The decoupling has made parameters related to human activities good predictors of water N:P stoichiometry in the East China Lake Region. Among the selected parameters, the population density and GDP are useful parameters in explaining the variance of N:P stoichiometry in East China Lake Region. While in other regions, N and P tend to respond to the selected parameters in a similar way, which made these parameters badly correlated with the N:P stoichiometry. With the progress of water management in China, we suppose a similar change of lake nutrients and their stoichiometry as developed countries is occurring, i.e., easier decrease of TP concentrations and continues increase of N:P mass ratios in the lakes. China has recently started to reform its water governance structure from administrative divisions to watershed divisions, known as "River Chief System" and "Lake Chief System". The results could help China to established more targeted water basin management policies under the context of the recent reform of water governance structure. According to the characteristics of nutrient stoichiometry and the underlining drivers of waterbodies from different catchments, specific nutrient management strategies should be developed in the future.

Acknowledgement

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Figure captions

Figure 1. Division of five lake regions in China; lake number and total surface areas (km^2) in each lake region;

Figure 2. TN concentrations, TP concentrations and TN:TP mass ratios from the monitoring sites;

Figure 3. Correlation analysis between water TN concentrations and TP concentrations in different lake regions;

Figure 4. Correlations between water TN:TP mass ratios and population density, cropland area and GDP values;

Figure 5. Changes of water nutrient concentrations (TN, TP and N:P mass ratios, respectively) during past three decades in China;

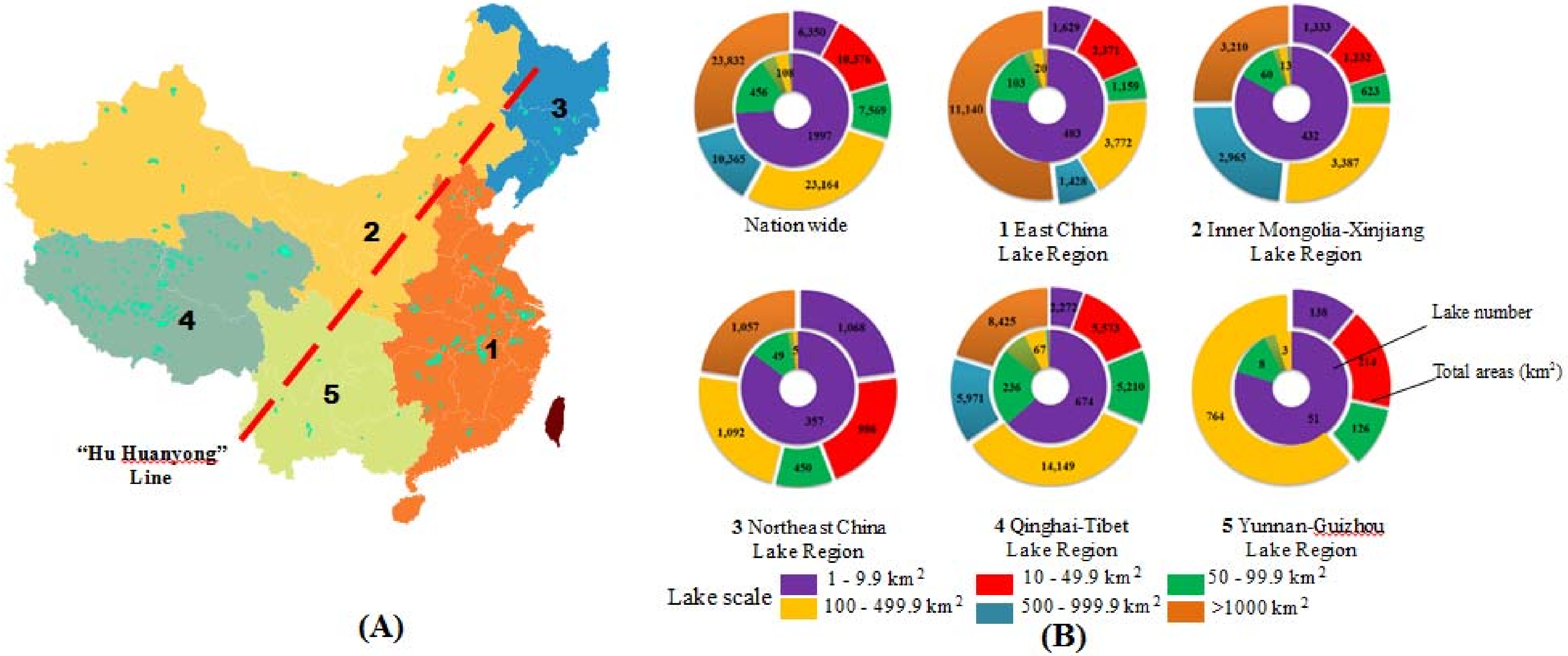


Figure 1. Division of five lake regions in China (A); lake number and total surface areas (km^2) in each lake region (B)

*1. East China Lake Region; 2. Inner Mongolia-Xinjiang Lake Region; 3. Northeast China Lake Region; 4. Qinghai-Tibet Lake Region; 5. Yunnan-Guizhou Lake Region. The lake with a surface area lower than 1 km^2 is excluded from this study. The information about lake number and surface area is obtained from Wang and Dou

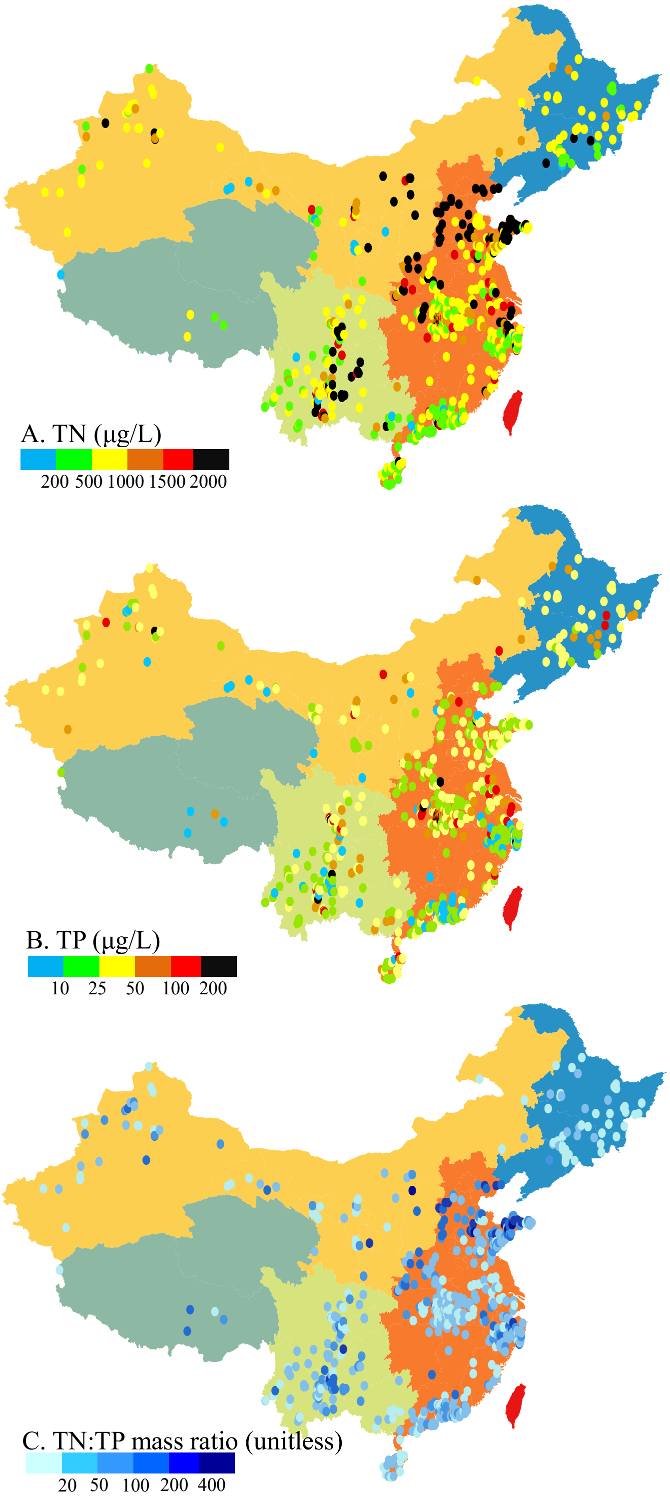


Figure 2. TN concentrations (A), TP concentrations (B) and TN:TP mass ratios (C) from the monitoring sites. Figure 2A and Figure 2B are revised from the figure from our previous publications (Tong et al., 2017b, c).

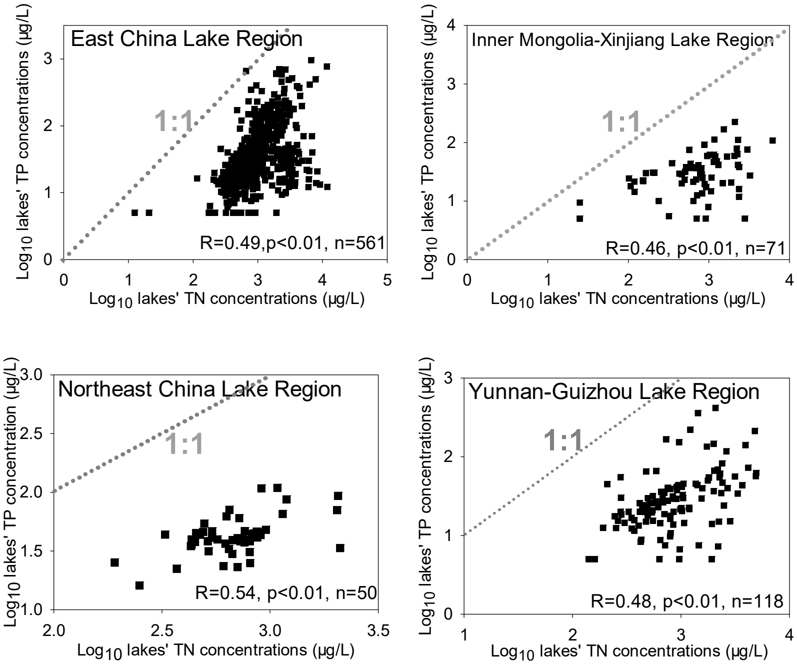
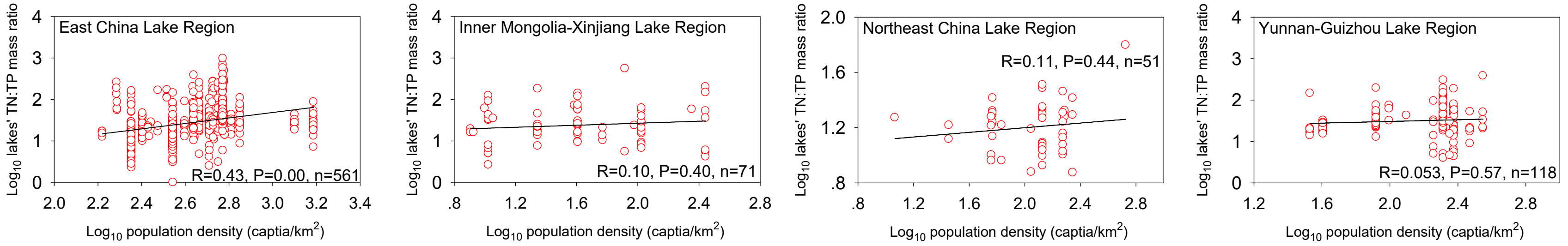
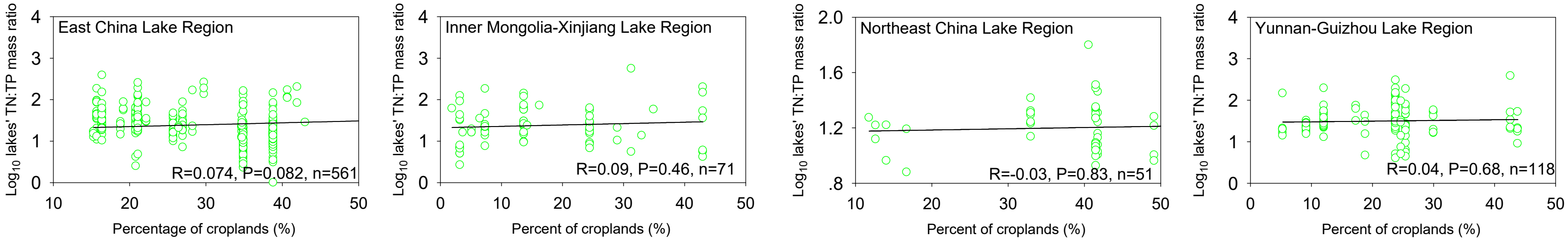


Figure 3. Correlation analysis between water TN concentrations and TP concentrations in different lake regions

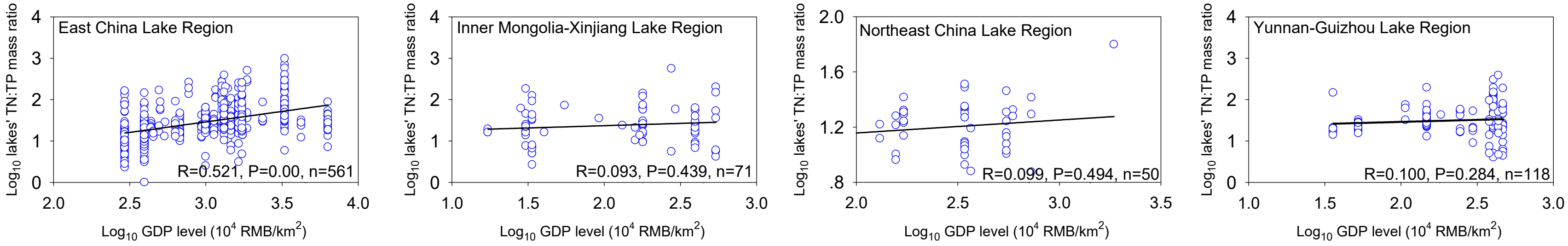
*The regression of TN and TP concentrations in the Qinhai-Tibet Lake Region is not shown due to the limited sampling sites.



A. Population density

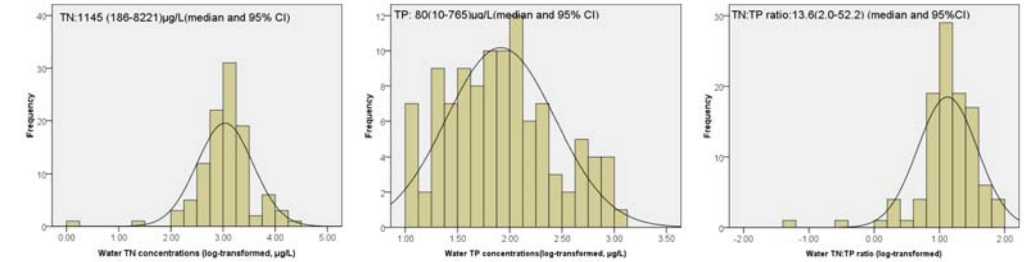


B. Cropland area

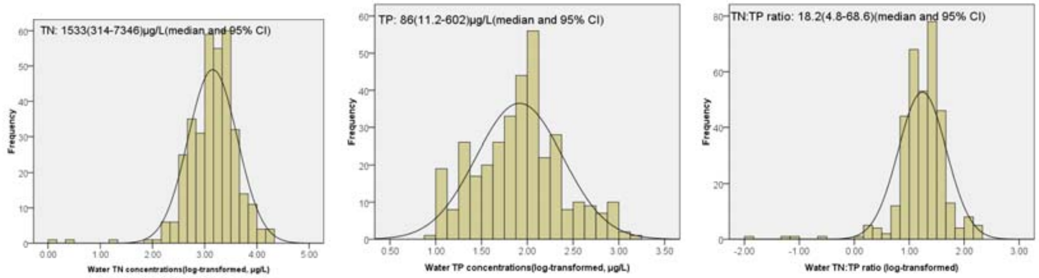


C. GDP values

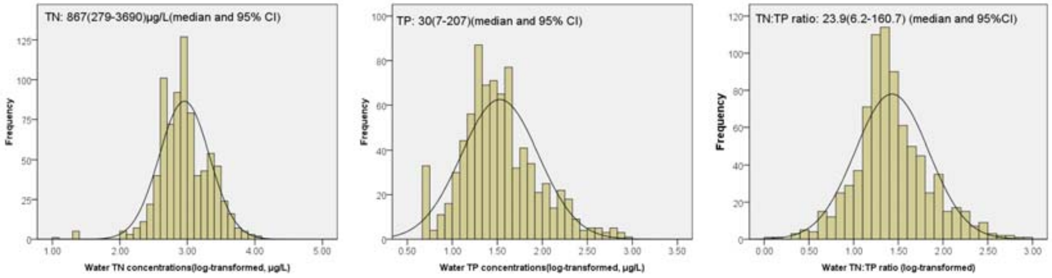
Figure 4. Correlations between water TN:TP mass ratios and population density (A), cropland area (B) and GDP values (C)


TN:1145 (186-8221)μg/L(median and 95% CI)
Frequency
0
10
20
30
40
0.00
1.00
2.00
3.00
4.00
5.00
Water TN concentrations (log-transformed, μg/L)
TP: 80(10-765)μg/L(median and 95% CI)
Frequency
0
2
4
6
8
10
12
1.00
1.50
2.00
2.50
3.00
3.50
Water TP concentrations(log-transformed, μg/L)
TN:TP ratio:13.6(2.0-52.2) (median and 95%CI)
Frequency
0
10
20
30
-2.00
-1.00
0.00
1.00
2.00
Water TN:TP ratio (log-transformed)

(A)


TN: 1533(314-7346)μg/L(median and 95% CI)
Frequency
0
10
20
30
40
50
60
0.00
1.00
2.00
3.00
4.00
5.00
Water TN concentrations(log-transformed, μg/L)
TP: 86(11.2-602)μg/L(median and 95% CI)
Frequency
0
10
20
30
40
50
60
0.50
1.00
1.50
2.00
2.50
3.00
3.50
Water TP concentrations(log-transformed, μg/L)
TN:TP ratio: 18.2(4.8-68.6)(median and 95% CI)
Frequency
0
20
40
60
80
-2.00
-1.00
0.00
1.00
2.00
3.00
Water TN:TP ratio (log-transformed)

(B)


TN: 867(279-3690)μg/L(median and 95% CI)
Frequency
0
25
50
75
100
125
1.00
2.00
3.00
4.00
5.00
Water TN concentrations(log-transformed, μg/L)
TP: 30(7-207)(median and 95% CI)
Frequency
0
20
40
60
80
100
0.50
1.00
1.50
2.00
2.50
3.00
3.50
Water TP concentrations(log-transformed, μg/L)
TN:TP ratio: 23.9(6.2-160.7) (median and 95%CI)
Frequency
0
20
40
60
80
100
120
0.00
0.50
1.00
1.50
2.00
2.50
3.00
Water TN:TP ratio (log-transformed)

(C)

Figure 5. Changes of water nutrient concentrations (TN, TP and N:P mass ratios, respectively) during past three decades in China

A. monitored values from a total of 106 lakes during 1988-1992; B. monitored values from a total of 347 lakes during 1995-2005; C. monitored values from a total of 800 lakes in 2014;

Table 1. Description of different variables in the catchments with lake sites (average and range).

Variables	East China Lake Region	Inner Mongolia-Xinjiang Lake Region	Northeast China Lake Region	Yunnan-Guizhou Lake Region
Land nutrient sources				
Farmland area (%)	39.2(15.3-76.7)%	17.8(1.9-43.0)%	35.8(11.8-74.0)%	22.7(5.3-43.8)%
Forest area (%)	39.8(0.5-75.9)%	14.2(0.7-39.6)%	50.5(13.9-82.2)%	48.8(28.5-72.0)%
Urban land use area (%)	8.0(1.3-22.6)%	1.6(0.3-4.2)%	3.5(0.4-9.5)%	1.2(0.2-2.6)%
Population density (capita/km^2)	480.6(166.1-1538.7)	70.3(8.1-277.6)	146.2(11.7-532.4)	176.8(33.9-353.3)
Gross Domestic Product value (10^4 RMB/km^2)	1564.4(294.2-6355.5)	163.5(17.3-542.3)	456.4(22.4-1860.6)	266.8(35.9-468.7)
Atmospheric nutrient sources				
Atmospheric N deposition (mg/(m^2.year))	3028.3(1043.9-5311.2)	885.8(255.2-2840.9)	1608.6(719.6-2460.0)	1876.3(464.0-2881.1)
Nutrient transport				
Annual precipitation (mm/km^2)	1189.3(473.0-1869.8)	351.1(92.6-900.1)	641.2(470.3-953.6)	1128.6(769.3-1568.7)
Area with severe soil erosion [a] (%)	8.1(0-44.8)%	40.3(7.0-79.4)%	4.5(0.9-9.8)%	18(0.7-35.5)%

a. The severe erosion is defined as the lands with a surface soil loss higher than 0.19 mm per year.

Table 2. Statistical results of water nutrient compositions in different regions

	Northeast China Lake Region (n=50)	Yunnan-Guizhou Lake Region (n=118)	Inner Mongolia-Xinjiang Lake Region (n=71)	East China Lake Region (n=561)
Total Nitrogen (μg/L)				
Median value	689.5	800.7	807.5	910.0
Mean value	749.6	1200.1	1068.3	1397.8
95% confidence level	291.8-2050.1	251.3-3690.5	71.0-2874.2	320.8-4001.3
1st quartile value	494.7	479.7	463.0	539.5
3rd quartile value	852.5	1741.4	1311.3	1767.7
Percentage based on different water quality standards				
Grade III limit in China [a]	88%	61%	63%	57%
Mesotrophic target in UK [b]	94%	73%	77%	72%
Grade III limit in Norway [c]	36%	35%	35%	29%
Total phosphorus (μg/L)				
Median value	40.5	25.9	30.0	30.2
Mean value	45.5	43.6	39.5	67.6
95% confidence level	22.7-100.0	6.6-153.7	5.0-111.7	8.0-231.8
1st quartile value	35.6	15.6	17.9	17.7
3rd quartile value	46.6	44.1	46.7	68
Percentage based on different water quality standards				
Grade III limit in China [a]	80%	80%	77%	64%
Mesotrophic target in UK [b]	2%	80%	28%	33%
Grade III limit in Norway [c]	2%	37%	28%	33%
TN:TP ratios (unitless)				
Median value	16.8	28.9	23	24.4
Mean value	17.5	46.4	44.5	47.6
95% confidence level	8.0-31.5	5.5-151.2	5-161.7	6.9-170.7
1st quartile value	11.6	20.4	10.4	15.8
3rd quartile value	20.3	51.1	53	43.6

a. TN and TP concentrations in China’s grade III limit are 1000 and 50 μg/L, respectively.

b. TN and TP concentration in UK’s mesotrophic target are 1500 and 20 μg/L, respectively.

c. TN and TP concentration in Norway mesotrophic target are 600 and 20 μg/L, respectively.

Table 3. Correlations between water nutrient concentrations and population density, GDP values and cropland area in the catchment (R and P values are shown)

Nutrient concentration [a]	Population density/ (captia/km^2) [b]	GDP values/ (10^4 RMB/km^2) [b]	Cropland area/ %
East China Lake Region			
TP	-0.36, p<0.001	-0.452, p<0.001	0.144, p=0.001
TN	-0.067, p=0.115	-0.081, p=0.056	0.434, p<0.001
Inner Mongolia-Xinjiang Lake Region			
TP	0.112, p=0.351	0.100, p=0.405	0.123, p=0.308
TN	0.236, p=0.047	0.262, p=0.027	0.231, p=0.053
Northeast China Lake Region			
TP	-0.041, p=0.778	-0.107, p=0.458	0.220, p=0.124
TN	0.011, p=0.938	-0.018, p=0.903	0.041, p=0.776
Yunnan-Guizhou Lake Region			
TP	0.353, p<0.001	0.334, p<0.001	0.373, p<0.001
TN	0.351, p<0.001	0.399, p<0.001	0.341, p<0.001

a. Water TN and TP concentrations are log-normal transformed in the correlation analysis.

b. Population density and GDP values in the catchment are log10 transformed in the correlation analysis.

Table 4. Correlation between water nutrients and driving variables in the catchment (R and P values are shown in the table).

Lake nutrient or nutrient stoichiometry	Forest area (%)	Urban area (%)	Livestock's manure (N, P (kg/ha) or N:P)	Precipitation (annual, mm)	Soil erosion area (%)
East China Lake Region					
TN:TP mass ratio	0.074, *p=0.082*	0.078, *p=0.063*	0.396, *p<0.001*	-0.125, *p=0.003*	0.057, *p=0.175*
TN (μg/L)	0.043, *p<0.001*	0.301, *p<0.001*	0.379, *p<0.001*	-0.568, *p<0.001*	0.521, *p<0.001*
TP (μg/L)	0.271, *p<0.001*	0.135, *p=0.001*	0.164, *p<0.001*	-0.296, *p<0.001*	0.285, *p<0.001*
Inner Mongolia-Xinjiang Lake Region					
TN:TP	0.089, *p=0.458*	0.117, *p=0.333*	0.131, *p=0.276*	0.066, *p=0.587*	-0.181, *p=0.131*
TN (μg/L)	0.231, *p=0.053*	0.313, *p=0.008*	0.206, *p=0.086*	0.206, *p=0.085*	-0.176, *p=0.143*
TP (μg/L)	0.123, *p=0.308*	0.360, *p=0.002*	0.060, *p=0.617*	-0.176, *p=0.143*	-0.110, *p=0.362*
Northeast China Lake Region					
TN:TP mass ratio	-0.031, *p=0.830*	0.170, p=0.239	-0.005, *p=0.971*	0.187, *p=0.192*	0.090, *p=0.534*
TN (μg/L)	0.041, *p=0.776*	0.321, p=0.019	-0.043, *p=0.767*	-0.379, *p=0.007*	0.203, *p=0.158*
TP (μg/L)	0.220, *p=0.124*	0.134, p=0.354	-0.114, *p=0.430*	-0.189, *p=0.188*	0.129, *p=0.373*
Yunnan-Guizhou Lake Region					
TN:TP mass ratio	0.038, *p=0.684*	-0.108, p=0.246	-0.351, *p<0.001*	0.126, *p=0.175*	-0.156, *p=0.091*
TN (μg/L)	0.341, *p<0.001*	-0.266, p=0.004	0.317, *p<0.001*	0.252, *p=0.006*	-0.072, *p=0.438*
TP (μg/L)	0.373, *p<0.001*	-0.248, p=0.007	0.358, *p<0.001*	0.196, *p=0.033*	0.059, *p=0.528*

Table 5. Importance of major drivers in explaining variances of water nutrients and their stoichiometry in the East China Lake Region[a]

TN/TP mass ratios	Relative importance/%	TN concentrations	Relative importance/%	TP concentrations	Relative importance/%
Precipitation	25.8	Precipitation	38.5	GDP values	45.6
Land soil erosion	23.0	Land soil erosion	21.1	Precipitation	13.5
GDP values	20.7	Cropland area	9.9	Forest area	11.8
N/P in livestock's manure	10.8	Forest area	8.8	Cropland area	11.6
Population density	5.5	Urban area	7.9	Population density	9.6
Forest area	3.6	GDP values	4.7	Land soil erosion	4.3
Total explained variances/%	**37.7**		**36.6**		**38.0**

a. Log_{10} transformed for water TN, TP concentrations and their mass ratios is applied in the GLM analysis.