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Impacts of Water Residence Time on Nitrogen Budget of Lakes and Reservoirs

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Abstract

As an important factor related to the self-purification capacity (e.g. denitrification, burial rate, and downstream output) in aquatic systems, water residence time (WRT) has great impacts on the nitrogen (N) dynamics and its removal process in lakes and reservoirs. In this study, we have analysed the impacts of WRT on the change rates of total nitrogen (TN) concentrations in 50 waterbodies (including 33 lakes and 17 reservoirs) in China, with different change trends (e.g. increasing trends and decreasing trends) and TN concentrations during 2012-2016. Based on the annual ecosystem-scale N mass balance, TN input and output flux in the waterbodies are estimated. The results showed that the decreases of TN concentrations usually occur in the waterbodies with the relatively high TN concentrations in 2012, and WRT has significant impacts on the TN change rates in the waterbodies. Longer WRT could slow down the TN increasing rates in the waterbodies acting as N sinks, but could accelerate the removal from the waterbodies acting as N sources. Higher water phosphorus (P) concentrations could also be beneficial for the faster N removal from the waterbodies. China has recently issued the “lake-chief” systems, addressing the specific and flexible strategies for water pollution control in different lakes. The self-purification capacity through denitrification and burial rate, which are closely related to WRT, should be taken into consideration when making specific water management plans in the future.

Keywords

Water residence time; nitrogen; ecosystem-scale mass balance; removal rate; lake and reservoir;

1. Introduction

Nitrogen (N) is one of the most important chemical elements for the plants and animals in the world (Vitousek and Howarth, 1991; Galloway et al., 2008; Suddick et al., 2013; Cui et al., 2013). In recent decades, N cycling in the terrestrial systems has been markedly accelerated due to intensive anthropogenic activities and increasing food demands (Galloway et al., 1995; Galloway et al., 2008; Tong et al., 2015). N utilized by human activities, usually in the form of N-containing fertilizers, is mainly fixed from the unreactive N_2 in the atmosphere through the Harber-Bosch reaction

(Vojvodic et al., 2014). However, not all the produced N-fertilizers have been utilized efficiently, and large quantities are discharged into aquatic systems (Cui et al., 2013). Human-induced nutrient discharge, including both N and phosphorus (P), has led to unexpected global water problems such as serious eutrophication and the formation of “dead zones” in waterbodies (Ryther and Dunstan, 1971; Smith et al., 1999; Anderson et al., 2002; Diaz and Rosenberg, 2008; Paerl, 2017). Water quality pollution and deterioration are especially an issue in China due to the rapid development in industry and agriculture during the past decades (Smith et al., 1999; Conley et al., 2009). The current N and P concentrations in many of China’s waterbodies still remain at high levels even after years of effort on pollutant control (Zhou et al., 2017; Tong et al., 2017a). In Taihu Lake, the water crisis caused by the extensive outbreak of harmful algal blooms (HABs) in 2007 severely affected the water supplies of millions of people for several weeks (Stone, 2011), and other freshwater lakes in China are also experiencing similar situations (Le et al., 2010).

Many previous studies have been carried out on the recognition and control of human-induced N discharges into aquatic systems (Xu et al., 2010; Cui et al., 2013; Liu et al., 2016). Excess N could come from agricultural fertilizer applications, residential sewages, industrial wastewaters, atmospheric depositions, etc. (Cui et al., 2013; Liu et al., 2016). Compared with P, N sources are more diffusive in the watersheds, increasing the difficulty in source quantification and control (Finlay et al., 2013). Strategies for the control of point and non-point N sources have also been widely developed to reduce the human-induced N discharges into waterbodies

(Ministry of Environmental Protection, China, 2015). For instance, Waste Water Treatment Plants (WWTPs) have been widely built in China, and they have been proven to be quite effective in the control of nutrient discharges into waterbodies (Tong et al., 2017a, b). So far, most of these efforts are devoted to the control of N transports from land to water, but after the N is discharged into the water, its removal process from the waterbodies could be only achieved by the function of the ecosystem itself, acting in a "self-purification capacity" (Finlay et al., 2013). Downstream outflows, denitrification, sedimentation and plant uptake in the aquatic ecosystems are believed to be the most important pathways to remove N from the waterbodies (Schlesinger, 2009; Finlay et al., 2013). Among all the internal removal processes, N removal from the water through denitrification is much higher than the loss through the sedimentation and plant uptake (Saunders and Kalff, 2001). For instance, in experimental wetlands in New Zealand, N removal by denitrification (3.0-3.3 g N/(m^2.d)) is far greater than either sedimentation (0.16-0.27 g N/(m^2.d)) or plant uptake (0.19-0.33 g N/(m^2.d)) (Oostrom, 1995).

With regard to the internal N cycling in the waterbodies, water residence time (WRT) plays a crucial role since it is related to almost all the natural processes (e.g. denitrification, sedimentation and downstream output) that could affect the nutrient concentrations in the waterbodies (Brett and Benjamin, 2008; Kõiv et al., 2011; Bruesewitz, 2012). Based on the nutrient input and output budget in the waterbodies, Finley et al. (2013) reported that the N removal efficiency through denitrification or the permanent burial in the waterbodies could increase significantly with the increase of WRT. A similar mechanism has also been observed for the P concentrations in the waterbodies, and the longer WRT could accelerate the settling down of particulate P from the water phase (Brett and Benjamin, 2008). For the organic carbons, Catalán et al. (2016) confirmed the negative relationship between the decay rates of dissolved organic carbon (DOC) and WRT across the aquatic systems. Evans et al. (2017) further confirmed that WRT could impose different impacts on organic carbon decays in the waterbodies acting as sources or sinks. For the waterbodies acting as carbon sinks, the longer WRT might be beneficial for the improvement of internal carbon removal efficiency, while for the waterbodies acting as the carbon sources, the longer WRT could accelerate the carbon loss (Evans et al., 2017). These studies confirmed the significant impacts of WRT on the internal nutrient (e.g. P and C) cycling in the waterbodies, but these impacts could also vary considerably among different nutrient types and waterbody types (i.e. nutrient sources or sinks).

As the human activities continue to alter the global nitrogen cycling, the ability to predict the WRT's impacts on the internal N cycling in the waterbodies is becoming more and more important. Internal N removal from the waterbodies is of particular interest because it is through the combined processes (e.g. denitrification, sedimentation and plant uptake) that the local and downstream N concentrations are related (Finlay et al., 2013). In this study, we have analysed the annual ecosystem-scale mass balance to explore the TN input and output budget in 50 waterbodies with different hydrological characteristics in China. Impacts of on to TN change rates in the waterbodies acting as N sinks or sources have been addressed. To identify the dominant processes in affecting the TN concentrations, TN input flux and output flux are estimated based on the annual ecosystem-scale N mass balance, respectively. The better understanding of the N removal pathway from the waterbodies is important to make effective management decisions to maintain and enhance the N removal processes in the face of agricultural intensification, urbanization and overall population growth that could increase the human-induced nutrient discharges into the water.

2. Materials and methods

2.1 Selected waterbodies

In this study, all of the water quality data are part of the randomized, unequally weighted probability surveys overseen by the Ministry of Environmental Protection, China, with the goal of creating unbiased assessments of water quality in the freshwater lakes across different provinces in China (Tong et al., 2017a, b). In detail, we have applied the following three guidelines during the selections of waterbodies. 1) With the continuous monitoring data, the lakes or reservoirs with over 40 continuous monthly TN monitoring points starting from 2012 have been selected. 2) The inclusion of various hydrological characteristics. To make the result representative, we have selected the lakes or reservoirs with different hydrological characteristics (considering lake depth, surface area, and water volume). 3) Large geographic coverage. We have selected the lakes or reservoirs in different regions to cover different climate conditions and economic development stages. In summary, a total of 50 freshwater waterbodies (including 33 lakes and 17 reservoirs, respectively), which are distributed in the 19 provinces in China, have been selected, and the detailed locations of the selected waterbodies are provided in Figure S1. Considering that the nutrient concentrations in the waterbodies could be easily affected by the human activities, the land use types (e.g. farmland, grassland, waterbody, built areas and desert), population density and annual precipitation in the belonging catchments have been summarized in Table S1. The division of catchments is provided by the Data Center for Resources and Environmental Sciences, Chinese Academy of Sciences, with data available at http://www.resdc.cn/ (shown in Figure S1). The hydrological conditions of the selected lakes and reservoirs are obtained from the Hydro Lakes database developed by the Global Hydro Laboratory (Messager et al., 2016) and reported values from Wang and Dou (1998). The detailed information for each waterbody, including WRT, surface area, water volume and water depth, respectively, has been provided in Table S2. In general, different sizes of waterbodies in China have been included, with the surface area ranging from 0.7 to 4,010 km^2 and with the water volume ranging from 0.6×10^8 to 290.5×10^8 m^3, respectively. WRT could also vary significantly among the different waterbodies, ranging from 10 days to 32 years.

2.2 TN monitoring data in the waterbody

The monthly TN concentrations in the 50 selected lakes or reservoirs have been collected from January 2012, to December 2016, and the data has been analysed to describe the variation trends during the study period. The field sampling is carried out based on the Technical Specifications Requirements for Monitoring of Surface Water and Waste Water in China (HJ/T 91-2002) (Ministry of Environmental Protection, China, 2002). The vertical water mixture samples are collected and mixed for each sampling site. Measurement of TN concentration in the water is based on the continuous flow analysis and N-(1-naphyl) ethylene diamine dihydrochloride spectrophotometry (HJ 667-2013), with the detection limit of 40 μg/L (Ministry of Environmental Protection, China, 2013).

2.3 TP monitoring data in the waterbody

To describe the impacts of TP concentrations on the decreasing rates of TN in the waterbodies, the monthly TP concentrations in the waterbodies in 2016 have been collected and the yearly average TP concentration is used in the further data analysis. An unfiltered aliquot of the surface water is prepared from each bulk sample. TP concentration is determined by persulfate digestion, followed by automated colourimetric analysis (ammonium molybdate and antimony potassium tartrate under acidic conditions) using a flow injection analyser, with a detection limit of 5 μg/L (Ministry of Environmental Protection, China, 2002).

2.4 TN input and output budget in the waterbody

The changes of nutrient concentrations in the waterbodies have been reported to be a first-order process (Brett and Benjamin, 2008; Evans et al., 2017). Hence, we use the ln-transformed TN concentrations in the regression analysis between the monthly TN concentrations and sampling time in the waterbodies, and the slope of the regression is defined as the average monthly TN increasing or decreasing rate ($month^{-1}$) during the study period. Accordingly, three typical categories of waterbodies have been defined as follows: TN sinks (with significant TN increases in the waterbodies, a positive slope and $p<0.05$), TN balance (without significant TN changes, $p>0.1$) and TN sources (with significant TN decrease in the waterbodies, a negative slope and $p<0.05$). The monthly change rate of TN concentrations in the waterbodies with significant TN changes is provided in Table S2. For the waterbodies with the significant TN changes, the ecosystem-scale mass balance for TN in the water phases of the lake or reservoir is described as follows (Vollenweider, 1975; Finlay et al., 2013):

$$V_{Waterbody} \times dC_{TN}/dt = M_{Total\ Input} - M_{Internal\ Removal} - M_{Downstream\ Output} \quad \text{Equation (1)}$$

where C_{TN} refers to the TN concentration in the water phase (mg/L), t is the time of the study periods (year), dC_{TN}/dt represents the yearly changes of TN concentrations in the water phase, $V_{Waterbody}$ refers to the water volume in the lakes or reservoirs, which is assumed to remain stable during the study period, and $M_{Total\ Input}$ (Mg/year) is the sum of all the TN loadings of the lakes or reservoirs through the upstream inflows, residential sewages, atmospheric depositions, etc. The N removal processes from the waterbodies have been further divided into two typical categories: loss through the downstream output ($M_{Downstream\ Output}$, Mg/year) and loss through the internal removal process ($M_{Internal\ Removal}$, Mg/year). The internal removal process represents all the processes that could remove N from the lake or reservoir water columns other than those through the outflowing rivers. The major N internal removal processes in the waterbodies include denitrification, permanent burial and plankton uptake (Finlay et al., 2013). Hence, Equation (1) could be further revised into Equation (2) and

Equation (3) for different waterbody types (Evans et al., 2017).

For the waterbodies acting as the N sinks, Equation (1) could be further revised as follows:

$$\ln\left(\frac{M_{T\_input}}{M_{D\_\mathrm{output}}+M_{I\_removal}}\right)=\frac{\ln(2)\times WRT}{TN_2} \qquad \text{Equation (2)}$$

For the systems acting as the N sources, Equation (1) could be further revised as follows:

$$\ln\left(\frac{M_{T\_input}}{M_{D\_\mathrm{output}}+M_{I\_removal}}\right)=-\frac{\ln(2)\times WRT}{TN_{1/2}} \qquad \text{Equation (3)}$$

where WRT refers to the water residence time in the selected waterbodies (years), and TN_2 or $TN_{1/2}$ refer to the doubling time or half-life of TN concentrations in the waterbodies (years), respectively (Evans et al., 2017). For the first-order process, TN_2 or $TN_{1/2}$ (years) in the water phases could also be calculated as follows:

$$TN_2\ or\ TN_{1/2}=\frac{\ln{(2)}}{k} \qquad \text{Equation (4)}$$

where k refers to the yearly increasing or decreasing rates of TN concentrations in the water phases ($year^{-1}$), which could be calculated based on the monthly TN concentrations from 2012 to 2016. Based on Equation (1) - Equation (4), the total TN input flux and output flux in the waterbodies could be estimated. A previous study containing over 80 waterbodies distributed worldwide has revealed a significant relationship between $M_{T\text{-input}}$ and $M_{I\text{-removal}}$ (as shown in Equation (5)) (Finlay et al., 2013):

$$\log M_{I\_removal}=-0.27+0.82\times\log M_{T_{input}} \qquad \text{Equation (5)}$$

Based on Equations (1) - (5), the doubling time or half-life (years) of TN concentrations, TN input or output ratio in the waterbodies and the flux through the $M_{Total\ Input}$, $M_{Downstream\ Output}$ and $M_{Internal\ removal}$ in the waterbodies (Mg per year) could be estimated accordingly.

3. Results

3.1 TN concentrations in the selected waterbodies

In 2016, the average TN concentration in all the 50 selected waterbodies is 1.11±0.75 mg/L (shown in Table 1 and Table S2), and this value is slightly higher than the Grade III limit (with a limit of 1.0 mg/L) set by China's water quality standard (Table S3). Large variations of TN concentrations among the different waterbodies have been observed (Table S2). For instance, the TN concentration in Xiaolangdi Reservoir in 2016 is 3.72±0.49 mg/L, while in Lugu Lake, the corresponding TN concentration is only 0.11±0.01 mg/L. We have compared the TN concentrations between the groups of lakes and reservoirs, but no significant differences between these two groups are observed ($p>0.05$). Based on the monthly TN monitoring data between 2012 and 2016, we find that 30 waterbodies out of a total of 50 waterbodies have significant increases or decreases in the TN concentrations (Table S2), while the other lakes or reservoirs do not have significant changes in the TN concentrations ($p>0.05$). Among the 30 waterbodies with the significant TN changes, TN concentrations have increased in 13 waterbodies during the study period, with an increasing rate of 0.001-0.017 month^{-1} (shown in Table 1), while TN concentrations have decreased in 17 waterbodies, with a decreasing rate of 0.003-0.027 month^{-1} (shown in Table 1). The largest monthly declining and increasing rates in the TN concentrations are observed in Yuqiao Reservoir and Nanyi Lake, which were 0.027 and 0.017 month^{-1}, respectively.

Figure 1 shows that the significant decreases in TN concentrations are usually observed in the waterbodies with the relatively high TN concentrations in 2012 (generally higher than 1.5 mg/L), while increases in TN concentrations are usually observed in the waterbodies with the low TN concentrations (generally lower than 1.0 mg/L). TN concentrations in the group with TN decreases during the study period (1.87 (0.50-4.15) (median value and range) mg/L) are significantly higher than the group with TN increase (0.65 (0.16-1.26) (median value and range) mg/L, p=0.00) and the group without significant TN changes during the study period (0.75(0.11-1.9 1) (median value and range) mg/L, p=0.00) (Figure 1). However, there are no significant differences in the TN concentrations between the increasing group and balanced group (p>0.05). We have also calculated the corresponding doubling and half-life of TN concentrations in the waterbodies based on the TN change rate (Table S2). For waterbodies with the TN decreases, most of the waterbodies have a half-life of less than 10 years. The minimum value is observed in Yuqiao Reservoir, with a value of 2.1 years, and the maximum value is observed in Xiaolangdi Reservoir, with a value of 19.3 years (Table 1). For the waterbodies with TN increases, most waterbodies have a doubling time over 5 years, with the maximum value of 41.3 years in Fuxian Lake and the minimum value of 3.4 years in Nanyi Lake. The longer TN doubling time indicates the slower increases of TN concentrations in the waterbodies.

3.2 Impacts of hydrological characteristics to TN concentrations

We have investigated the relationship between the seasonal variations of TN concentrations in the waterbodies and the corresponding hydrological characteristics, including altitude, surface area, lake depth and water volume of the waterbodies, respectively. The seasonal variation of TN concentration is evaluated as the TN standard deviations during the 12 months divided by the TN average concentration during the year, and the monthly TN monitoring data in 2016 is analysed in detail. The results show that waterbody altitude ($p<0.05$, $n=48$), depth ($p<0.01$, $n=48$) and water volume ($p<0.1$, $n=48$) could be effective in reflecting the seasonal variations of TN concentrations (as shown in Figure 2), while water surface area is not a good indicator ($p>0.1$, $n=48$). Higher seasonal variations could usually occur in the low-altitude regions, while the deeper depths and larger water volumes in the waterbodies could mitigate the seasonal TN changes. In China, the waterbodies with lower altitude are usually located in the regions with the significant anthropogenic activities and economic development (Tong et al., 2017a). The changes of human-induced nutrient discharge could possibly cause the large seasonal variation of TN concentrations in the waterbodies, while the larger water volume and deeper depth means the waterbodies have the larger capacity to dilute the pollutant inputs from the human activities, leading to the smaller TN seasonal variations.

In Figure 3, we investigated the relationship between WRT and the TN change rates in the waterbodies during the study period. The results show that the WRT in the waterbodies could also impose significant impacts on the increasing or decreasing rates of TN concentrations, but these impacts could be different between the groups acting as TN sinks or sources, respectively (Figure 3). For the waterbodies with the TN increases during the study period, an increase in the doubling time of the TN concentrations could be observed with the longer WRT ($p<0.05$, $Y=0.92X+8.12$, $n=13$, Figure 3A). However, for the waterbodies with the TN decreasing, a shorter half-life of TN concentrations in the waterbodies is observed with the longer WRT ($p<0.05$, $Y=-0.40X+8.77$, $n=17$, Figure 3B). This point addresses the importance of differentiating the waterbody types when assessing the WRT's impacts on N concentration changes in the waterbodies. Generally, with a 10-year increase in WRT, the doubling time or half-life of TN concentrations in the waterbodies will increase and decrease by approximately 9.2 and 4.0 years, respectively. In addition to the waterbodies' hydrological characteristics, we also found that the higher water TP concentrations could probably accelerate the TN removal rates from the waterbodies, and the higher monthly TN decreasing rates are observed in the waterbodies with the high TP concentrations (Figure 4). Based on the regression relationship (Figure 4), if with the water TP concentrations increase by 10 μg/L, the monthly decreasing rates of TN concentrations in the waterbodies could increase by ~5 μg/L (as shown in Figure 4).

3.3 **TN input and output flux in the waterbody**

The change of TN concentrations in the waterbodies is caused by the changes of TN input and output flux in the waterbodies (Finlay et al., 2013). Based on the annual ecosystem-scale N mass balance, we have estimated the TN input and output fluxes in the selected waterbodies. The results have shown that large variations in the TN input and output ratios are observed among the waterbodies, leading to different changes of TN concentrations in the waterbodies. For the waterbodies with TN increasing, the TN input and output ratio could be 1.06 (1.00-2.12) (median and range), while for the waterbodies with TN decreasing, the corresponding ratios could be 0.88 (0.07-1.00) (median and range). The lowest TN input and output ratio (0.07) is observed in the Yuqiao Reservoir, and lower ratios could indicate the effective control of nutrient discharges from human activities to the waterbodies (Tong et al., 2017a).

The total TN input and output fluxes into or out of the waterbodies with the significant TN changes during the study period have been calculated accordingly, and the results are provided in Figure S2. Generally, the TN input and output flux could vary significantly among different waterbodies, ranging from 2.4 to 2.5×10^5 Mg/year, and from 8.8 to 2.5×10^5 Mg/year, respectively. Based on the input and output budget for each waterbody, we have calculated the net changes of TN budget in the water column. In the waterbodies with the TN increasing, there are 101.7 (10.6-1472.9) (median and range) Mg of net TN accumulations, while for the waterbodies with TN decreasing, there are 231.0 (1.2-2832.0) Mg of net TN losses from the waterbodies. Normalized by the surface area of waterbodies, the total TN input and output rates in the waterbodies are shown in Figure 5. Significant variations of TN input and output rates exist among different types of waterbodies. For the TN decreasing group, the TN input fluxes could range from 0.1 to 2480.3 g/(m^2.year), while for the TN increasing group, the TN input fluxes could range from 0.5 to 104.8 g/(m^2.year). It should be noted that the extreme high TN input flux is observed in the Xiaolongdi Reservoir (with a value of 2480.3 g/(m^2.year)), which could be attributed to the high TN loadings from the upstream water and severe soil erosions in the Loess Plateau (Ju and Li, 2017; Li et al., 2017). For the TN increasing group, the highest TN input flux is observed in Poyang Lake, with a value of 104.8 g/(m^2.year). The TN output fluxes range from 0.3 to 104.0 g/(m^2.year) for the TN increasing waterbodies, while they range from 0.4 to 2506.7 g/(m^2.year) for the TN decreasing waterbodies.

4. Discussion

4.1 Changes of TN concentrations in the waterbody

Despite the decade's efforts on the water pollution controls in China (Tong et al., 2017a), a strong argument about the recent changes and current situation of China's water quality (i.e. continuous deterioration or improvement in some regions) still exists (Zhou et al., 2017). A survey including over 800 of China's lakes in 2014 reveals that TN concentrations in the lakes of China are still high, with an average concentration of 1337±1489 μg/L. Approximately 20% of all these sampling sties have TN concentrations higher than 2000 μg/L, which is the Grade V limit of China's surface water standards. On the other hand, only ~3% of them have TN concentrations lower than 200 μg/L (Grade I limit by China's surface water standard) (Tong et al., 2017b). Similar conditions also exist for P, another essential element for the organisms (Tong et al., 2017a). The Environmental Kuznets Curve has noted that the environmental quality in a region first deteriorates during the initial period of economic development, but that the environmental quality will improve at later stages due to continuous investment in environmental protection and sanitation improvements (Grossman and Krueger, 1993). There is no doubt about the huge achievement of economic development in China since the reform and opening up in the 1980s, while the recent trend of China's water quality change is still not clear. Compared with the rivers or open oceans, lakes or reservoirs could be more easily affected by the pollutant discharges from human activities (Piña-Ochoa and Álvarez-Cobela, 2006), and they are also more difficult to recover to a good ecological status. Many previous studies reported serious water pollution in China in the earlier periods (mainly before the year of 2005) (Smith et al., 2003; Conley et al., 2009; Stone, 2011; Tong et al., 2017c). In this study, we find that 37 waterbodies, out of a total of 50 selected waterbodies, have decreased or remained stable in TN concentrations during the study period (Table 1 and Table S2), and only 13 waterbodies have had significant but slow increases (with a median value of 0.007 month^{-1}). Compared with the TN decreasing rates, the increasing rates in the waterbodies are relatively slow. Monthly TN decreasing rates in the waterbodies could be as high as 0.027 month^{-1} (Table 1 and Table S2). We have previously reported that quick declines of water TP concentrations have occurred in many of China's waterbodies, although this decline in rates could vary significantly between different regions (Tong et al., 2017a). Zhou et al., (2017) have also demonstrated the water quality improvement measured by the ammonium concentrations and chemical oxygen demands due to the enormous investment on the environmental remediation in China. Water nutrient declines usually occur after the shifting of major sources, especially the pollutant reductions brought by the quick improvement of urban and rural sanitation in recent years (Tong et al., 2017a). This study also shows that significant improvements in water TN concentrations may have occurred. The improvement of TN concentrations has demonstrated the effectiveness of water management strategies during the past years, but there is also a need for more specific and flexible strategies in water pollution control in the future, since different waterbodies could have different changes of TN concentrations.

4.2 Role of waterbodies' self-purification capacity to TN changes

Currently, most efforts on water pollution control have been devoted to the cutting of pollutants discharges from human activities to aquatic systems, i.e. building of WWTPS, toilet improvement in the rural areas and reduction in the usage of agricultural fertilizers (Tong et al., 2017a; Cui et al., 2018). There is no doubt about the importance of pollutant reduction in waterbodies (Zhou et al., 2017; Tong et al., 2017a). As previous studies reported, the nutrient discharges into waterbodies from intense human activities have been mainly responsible for the sharp increases of nutrient concentrations and the deterioration of water quality (Vörösmarty et al., 2010). However, after the pollutants are discharged into the water, the self-purification capacity of the waterbodies is crucial to mitigate the negative impacts of increased human N inputs (Finlay et al., 2013; Saunders and Kalff, 2001) because it is not feasible to treat the polluted water by using engineering measures as we have done for urban sewage. For the N removal, the self-purification capacity of the aquatic systems could include the downstream outflows, denitrification, sedimentation, plant uptake, etc. (Schlesinger, 2009; Finlay et al., 2013). As the index reflecting the water cycling rate in the aquatic systems, WRT is related to almost all these processes (Oostrom, 1995; Saunders and Kalff, 2001; Seitzinger et al., 2006). Different nutrient changes in response to the WRT in different types of waterbodies could possibly indicate the difference in the nutrient input flux and removal process (Finlay et al., 2013).

In this study, we find that the WRT in the waterbodies could impose significant impacts to the TN change rates (Figure 2). For the waterbodies with a TN increase, the longer WRT could accumulate the TN concentrations much slower (reflected as the longer doubling time of TN), but for the waterbodies with TN decreases, the longer WRT could reduce the TN concentrations faster (reflected as the shorter half-life, as shown in Figure 3). This trend is quite consistent with the decay rate of organic carbons in the waterbodies (Evans et al., 2017). It has been reported that the ecosystem N removal efficiency via denitrification or permanent burial is primarily affected by the water residence time, with the longer residence times resulting in increased removal efficiency (Saunders and Kalff, 2001). For instance, in experimental wetlands in New Zealand, the total N removal through denitrification was 1095-1205 g/(m^2.year), occupying the majority of the total internal loss (Oostrom, 1995). N removal efficiency through the internal processes could increase from 4% to 20% of the total input fluxes if WRT of the waterbody increased from 0.2 years to 1 year (Finlay et al., 2013). The internal processes in the lakes can even remove a large percent of TN inputs from the surrounding watersheds, providing important benefits for the water quality in the downstream ecosystems. Hence, the internal N loss strengthened by the increase of WRT could possibly cause the slower TN increases in the TN-increasing waterbodies, but the quicker TN decreases in the

TN-decreasing waterbodies (as shown in Figure 3).

To further identify the contributions of the internal removal process and downstream output in the TN changes of waterbodies, Figure 6 has specified the TN output flux through the internal removal and downstream output, respectively. For the TN decreasing waterbodies, TN output fluxes through the internal removal and downstream output are 2.9 (0.1-326.2) and 8.3 (0.2-2180.5) g/(m^2.year) (median value and range), respectively. For the TN increasing waterbodies, the TN output fluxes through the internal removal and downstream output are 6.1 (0.3-24.4) and 9.2 (0-79.7) g/(m^2.year) (median value and range), respectively. It is clear that in different types of waterbodies, the TN output flux through the different processes could be different. For the waterbodies with TN decreases, the TN output flux through downstream output could be 1.5-16.7 times as high as the output flux through the internal removal processes. For the waterbodies with TN increases, the TN output flux through the internal removal process is much higher than the downstream output fluxes, which could occupy 39%-100% of the total TN input fluxes into the waterbodies (Figure 6). It has been reported that annual denitrification in the aquatic environments is quite different among the ecosystem types (Piña-Ochoa and Álvarez-Cobelas, 2006), and the highest denitrification rate is observed in the lakes (1.4-52.1 g/(m^2.year)) and rivers (15.4-49.6 g/(m^2.year)) compared to the coastal ecosystems (1.3-15.4 g/(m^2.year)) and estuaries (0.3-11.8 g/(m^2.year)) (Piña-Ochoa and Álvarez-Cobelas, 2006). Generally, our predicted values of TN output through the internal processes were quite consistent with the field measured values in other waterbodies

(Figure 6).

We acknowledge the significance of N internal removal process in the changes of TN concentrations in the waterbodies. However, there are some other factors that should also draw the attention of managers in water TN controls, such as TP concentrations. TP in the waterbodies has a coupling relationship with the TN decreasing rate, as shown in Figure 4, and this relationship indicates that the higher TP concentrations in the waterbodies could accelerate the TN removal process from the waterbodies (Bernhardt, 2013). This point is also demonstrated in the whole-ecosystem experiments in Norway and the United Kingdom, where additions of P fertilizers could increase the N removal efficiency in both lakes and streams (Davison, 1995; Kaste and Lychesolheim, 2005), and this provided direct evidence for the role of P as an important control over the N cycling and fate in the freshwater ecosystems. The observed impacts of P concentrations on the TN removal process in the waterbodies is mediated via the coupled processes regulating the transfer of N from the water column to anoxic sediments (Small et al., 2014) that promote the permanent N losses through denitrification (Saunder and Kalff, 2001). In the high-P lakes, algal blooms efficiently move large amounts of N and P together with recently fixed algal carbon into the subsurface, fuelling high microbial activity and oxygen consumption. The high supply of carbon, together with low oxygen, provides ideal conditions for denitrification, the microbial metabolic pathway in which microbes breathe nitrate (NO_3^-) while decomposing organic substrates, converting NO_3^- to N_2(Schindler, 2012) (Tartari and Biasci, 1997).

4.3 Implication for China’s future water management

In the years 2017 and 2018, China issued the “river-chief” and “lake-chief” systems in water management, which address the more specific and flexible strategies for water pollution control in the rivers and lakes, respectively (China's State Council, 2017, 2018). This improvement in water management indicates that the managers have realized the limitations of a unified, national-scale policy on the control of water pollution in different regions. As the most important factor in determining the self-cleaning of nutrients in the waterbodies, in future water management, the impacts of WRT on the nutrient changes in the waterbodies should be addressed. For instance, the effluents from wastewater treatment plants should be first discharged to constructed wetlands to increase the WRT and improve the N removal efficiency before the effluents are discharged into aquatic systems. The different types of waterbodies, acting as nutrient sinks or sources, should be addressed separately when discussing the impacts of WRT to changes of water TN concentrations. The coupling relationship between the TN decreasing rates and water TP concentrations also requires serious thinking on a suitable pace of N and P reductions in the waterbodies. So far, most of our efforts on water pollution control have been devoted to the reduction of human-induced pollutant discharges into the waters, such as the building of WWTPs and sanitation improvement in the rural regions. This strategy has been proven to be effective based on recent changes of water qualities, without considering the large building and running costs of such facilities. However, currently, the high percentage of urban wastewater treatment has already been achieved in most of the populated regions (with a treatment percentage of approaching or over 90%), and the further reduction of pollutants (i.e. TN and TP) through sanitation improvement in urban areas is quite limited (Tong et al., 2017a,b). Hence, maybe now is the right time to reconsider the role of the self-purification capacity in the waterbodies to further reduce the pollutant levels.

5. Conclusions

In this study, we have analysed the impacts of WRT on the change rates of TN concentrations in 50 waterbodies (including 33 lakes and 17 reservoirs, respectively) in China during 2012-2016. The 50 waterbodies were grouped into three categories depending on whether TN concentrations are increasing, decreasing or stable over the study period. The results show that the average TN concentrations in the waterbodies with decreasing TN (1.87 (0.50-4.15) mg/L) are significantly higher than the waterbodies with increasing TN (0.65 (0.16-1.26) mg/L, p=0.00) and the waterbodies with stable TN during the study period (0.75 (0.11-1.91) mg/L, p=0.00). For the waterbodies with TN increases, an increase in the doubling time of TN concentrations could be observed with the increase of the WRT. However, for the waterbodies with TN decreases, a shorter half-life of TN concentrations in the waterbodies is observed with the longer WRT. In addition, higher TP concentrations could also be beneficial for the removal of TN from the waterbodies. Based on the annual ecosystem-scale N mass balance, the TN input and output flux in the selected waterbodies have been calculated, ranging from 2.4 to 2.5×10^5 Mg/year, and from 8.8 to 2.5×10^5 Mg/year, respectively. In China's future water management, the self-purification capacity through denitrification and burial rate, which are closely related to the WRT, should be taken into consideration when making specific management plans.

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