Science of the Total Environment 645 (2018) 1212–1220

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Effects of anthropogenic activities on long-term changes of nitrogen budget in a plain river network region: A case study in the Taihu Basin

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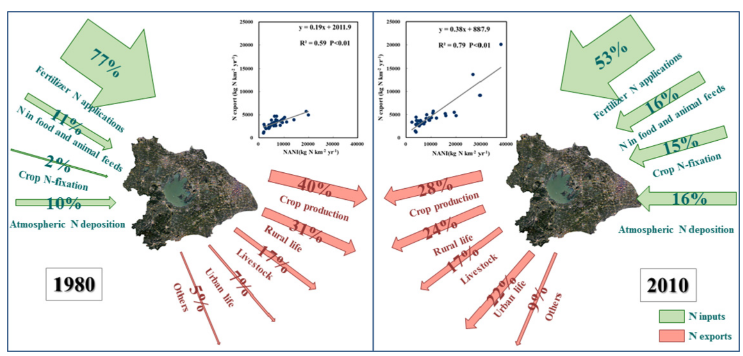
HIGHLIGHTS

- Both inputs and exports of N increased substantially during the study period.
- The NANI method and the ECM are first integrated to assess N load in a basin.
- Urbanization, economic/population growth are key factors of spatial-temporal changes.
- The contribution of agricultural source to N exports was decreased.
- Destruction of the N balance of the ecosystem is investigated in the Taihu Basin, China.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 February 2018
Received in revised form 28 June 2018
Accepted 28 June 2018
Available online 21 July 2018

Editor: G. Ashantha Goonetilleke

Keywords:
Nitrogen budget
Non-point source pollution
Anthropogenic activities
Eutrophication
Export coefficient model
Taihu Basin

ABSTRACT

Over recent decades, Taihu Lake, the third largest freshwater lake in China, has borne the brunt of intensive human activities. Non-point source pollutants and discharges of domestic wastewater are now the main cause of eutrophication. To control non-point source pollution, it is useful to have a good understanding of the spatial and temporal distribution of N (nitrogen). In this study, we applied Export Coefficient Model (ECM) and the Net Anthropogenic Nitrogen Inputs (NANI) method to estimate the N loads in the Taihu Basin at county scale since 1980. We found that N inputs and exports had increased from 6432 and 3170 kg N km^{-2} yr^{-1} in 1980 to 9722 and 4582 kg N km^{-2} yr^{-1} in 2010, respectively. The 151% increase of N inputs, but 144% increase of riverine N outputs suggested the more N was retained within the Taihu Basin. Both the population density and the urban areas were strongly correlated with N inputs and exports. Approximately 38% of the N inputs were exported in 2010, but only 19% were exported in 1980. This ratio illustrated that human activities, especially urbanization and population growth, have upset N budget in the Taihu Basin. This study supported by empirical models provides a case to demonstrate the N cascade in the Taihu Basin and can also be used to support decision making and to facilitate the development of measures to control N in the future.

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https://doi.org/10.1016/j.scitotenv.2018.06.354
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1. Introduction

Over the last 30 years, since the reform and opening-up (Economic Reform and Open-Door Policy in China), China has experienced rapid economic and social development and has transitioned from a mainly rural to an increasingly urban society; indeed, urbanization increased from 19.4% in 1980 to 49.7% in 2010 (Jian Xinhua, 2010; Xie et al., 2017). Over-exploitation and excessive use of natural resources during this period has resulted in severe deterioration of lake ecosystems and pollution of water bodies (Qin et al., 2007; Xia et al., 2016), and the area of eutrophic lakes in China increased from 600 km^2 in 1980 to 14,000 km^2 in 2010 (Ma Ronghua, 2011). Eutrophication threatens the safety of natural ecosystems and the quality of drinking water (Hobbie et al., 2017), and its occurrence has far-reaching consequences for human welfare. It has been previously reported that N is the main contributor to eutrophication of freshwater environments (Carpenter et al., 1998; Poor and McDonnell, 2007; Wang et al., 2017). It generally leads to algal blooms, reduced biodiversity, unsafe drinking water and the destruction of water ecosystems (Wan et al., 2014; Goyette et al., 2016). Excessive nitrogen inputs to river basins reflect increases in anthropogenic activities; for example, Galloway et al. (2003) reported that N yield had increased nearly tenfold since 1860 because of human activities (Galloway et al., 2003). Human activities, including agriculture, forestry, fishing, animal husbandry, mining, transportation and constructions and more, are generally necessary for our survival and contribute to improved living standards. However, because of the unreasonable rate at which human society has developed recent decades, human activities have caused environmental degradation and, in particular, eutrophication of water bodies. Therefore, it is urgently need to improve our understanding of the relationships between human activities and N pollution in water bodies (Johnes, 1996).

To date, numerous studies have examined the relationships between N cycling and various human activities (Howarth et al., 1996; Y. Chen et al., 2016; D. Chen et al., 2016). N inputs and exports are the two vital parts of N cycling. The N export ratio, the ratio of N exports to N inputs, reflects the capacity for N retention in watershed ecosystems and the potential risks of N pollution (McIsaac et al., 2001; Huang et al., 2016). The ability of a basin to retain N determines how much of the N that entered the basin will be subsequently exported via the river systems, and is measured at the basin scale by the N export ratio. The N export ratio varies widely among watersheds. A review showed that N export ratio ranged from 3% to 118%, with an average ratio of 24% (Zhang et al., 2014), and it is influenced by hydroclimate, land use type, the degree of N saturation, and human activities (Howarth et al., 2012). Previous studies have shown that approximately 25% of the NANI of 154 watersheds in the US was exported to river systems (Howarth et al., 2012), 20%–25% was exported in North America and Europe (Howarth et al., 2006), and 30%–51% was exported from 49 watersheds in Taiwan (Huang et al., 2016). However, few researchers have explored how this ratio changes in a watershed that has experienced rapid social and economic development. Also, there have been few studies of how N cycling and the N balance vary over time because of human activities (Gao et al., 2015; Goyette et al., 2016).

Adopting suitable methods to estimate the N load is the key in this study. The Net Anthropogenic Nitrogen Inputs (NANI) method, first introduced in 1996 (Howarth et al., 1996), has been widely used to estimate the major sources of anthropogenic N inputs in watersheds with areas of between 16 and 279,000 km^2 in the U.S, UK, China, Sweden, France, India and Belgium (Howarth et al., 2012; Zhang et al., 2015; Y. Chen et al., 2016; D. Chen et al., 2016; Gao et al., 2016; Zhang et al., 2016). Increases in N inputs are generally accompanied by corresponding increases in N exports (Howarth et al., 1996), which directly cause eutrophication and destroy water systems (Hollinger et al., 2001). Therefore, N exports need to be assessed when evaluating the interactions between human activities and N cycling. Recent studies have explored the relationships between anthropogenic N inputs and riverine N exports (Huang et al., 2016). However, because of the challenges associated with measuring riverine N exports at the watershed scale, it is generally difficult to obtain sufficient data for such studies. Models can be used to simulate N exports from basins where there is insufficient monitoring data. Many process-based physical models do not give good results for areas of flat terrain and complex crisscross river systems found in plain river network areas like the Taihu Basin (Lai et al., 2016). Therefore, to simulate the N exports from the Taihu Basin, we chose a very robust empirical model, namely Export Coefficient Model (ECM), which was developed in North America in the 1970s to estimate pollutant export load. This model can resolve the issues associated with the flat terrain and complex river network and can be used to predict N exports from river basins (Lu et al., 2013; Worrall et al., 2012; Li et al., 2016; Shih et al., 2016), assess the influence of land use on N loads, predict annual nutrient inputs to lakes and rivers (Johnes, 1996). The NANI method and the ECM can be integrated to assess N budget and the corresponding risks of N retention.

The Taihu Basin has experienced rapid rates of urbanization and economic growth in recent decades and is a representation of modern developed area in China. Algal blooms that thrive in the eutrophic conditions threaten the safety of the drinking water supply and even entire ecosystem of the lake. We believe that, if we had reasonable estimates of the N budget, this challenge can be handled. The main goal of this study was to investigate temporal variations, and environmental implications of N inputs and exports in the Taihu Basin caused by anthropogenic activities. The specific objectives were to (i) estimate N inputs to, and exports from, the Taihu Basin; (ii) identify the impact of human activities on N balance; (iii) assess the ecological and environmental problems that might result from excessive N in the basin. We used two empirical models to estimate N inputs and exports, and then we explored the N budget and N retention risks. We also considered the factors that contributed to the changes of N export ratio. The findings of this study will support improved long-term water resource management and land use planning, and will reinforce the need for eco-environmental protection in many basins that are severely affected by anthropogenic activities.

2. Materials and methods

2.1. Study area

In this study, we evaluated the effects of anthropogenic activities on N budgets at the watershed-scale over a 30-year period in the Taihu Basin, which is situated in the Yangtze River Delta, Eastern China (106°7′-121°47′ E, 24°30′-33°54′ N; Fig. 1). The basin extends over an area of 36,895 km^2 and covers all or part of 45 counties in Jiangsu and Zhejiang Provinces, and the Shanghai Municipality. Taihu Lake is situated in the center of the basin, and it is the third largest freshwater lake in China, with a surface area of 2338 km^2 and a mean water depth of 1.9 m. The basin is characterized by a humid subtropical climate with classic monsoon seasons. It has an annual mean temperature of 16 °C, and the annual precipitation of 1115 mm (Xia et al., 2016; The health status report of Taihu Lake, 2010), and more than 60% of the annual precipitation falls from June to September. The Taihu Basin is a plain river network region that has flat landscape, abundant rainfall, and dense river system. More than 200 rivers connect to the Taihu Lake (Lu et al., 2012), and the total length of channels in the Taihu Basin is 12,000 km (Fig. 1) (Qin et al., 2007).

The Taihu Basin is one of the most industrialized and urbanized regions in China. According to official statistics, the basin had a population of 51.76 million in 2010, of which 72% lived in urban or suburban areas, and the per capita GDP in the Taihu Basin was 2.9 times higher than the national average (Bureau of Taihu Lake Basin, 2010). In 2010, cultivated land covered 17,237 km^2 of the Taihu Basin and agriculture was dominated by a rice-wheat rotation. Agriculture is relatively intensive, and, while the total area of the basin accounts for only 0.4% of China, 1.3%

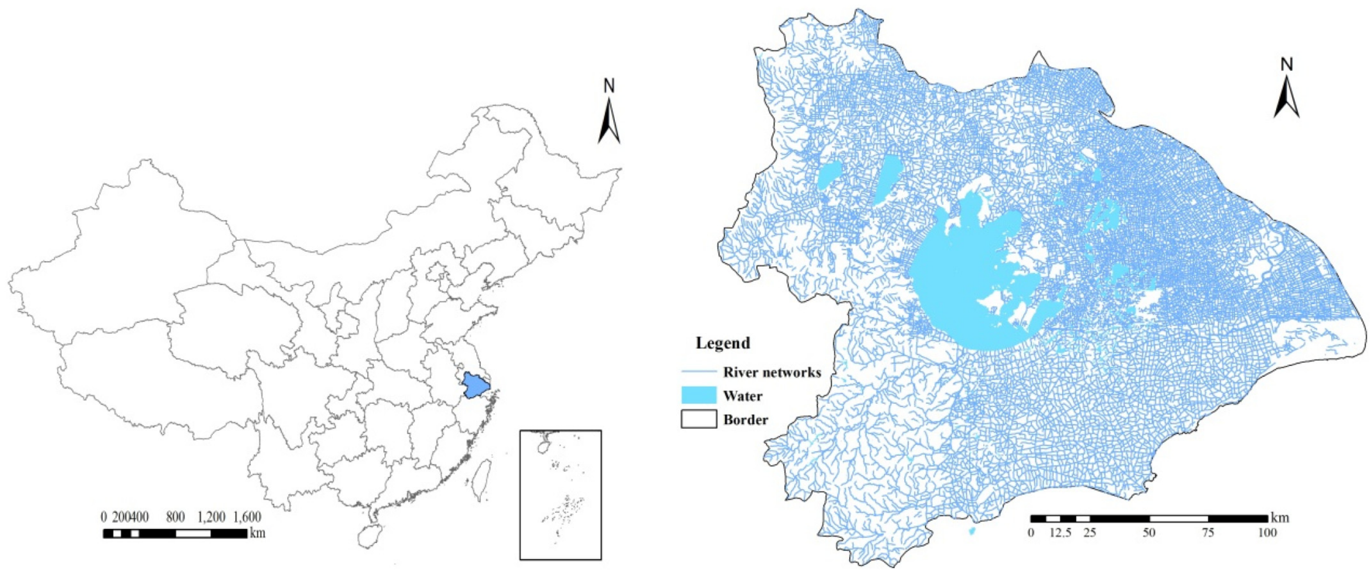

Fig. 1. Map showing the Taihu Basin and the river network. The river network is on an extensive plain, and comprises both well-developed rivers and artificially-excavated channels.

of the total amount of fertilizer used in China is consumed in this area. Rapid development over the last three decades has had a series of consequences for the environment. Of these, the serious pollution of Taihu Lake poses a threat to the safety of the region's drinking water supply. The authorities have been taking measures to tackle the water pollution since the late 1990s and, for example, factories in the basin have to treat wastewater as outlined in regulations before discharging it into rivers and the water quality of all rivers that discharge to Taihu Lake has to meet Grade III of the National Standards (National Surface Water Quality Standard GB3838-2002) (Qin et al., 2007). Even with these measures, the pollution of Taihu Lake is still severe in recent years.

We examined the impact of human activities on variations in N by analyzing the relationships between N inputs, exports and the cultivated and construction land proportions (%), urban population as a % of the total population, population density, and GDP per unit area in 45 counties in 2010. We found that cultivated land in these counties ranged from 5.47% to 81.44%, and construction area ranged from 4.11% to 95.39%. The urban population percentage ranged from 1.07% to 90.66%. The population density was between 169 and 8179 person/km^2. The GDP per unit area ranged from 9.25 to 1225.64 million yuan/km^2. The above parameters varied widely between counties and so can represent variations in the inputs and exports of N for different stages of development or different levels of human activity across the basin.

2.2. Land use change in the Taihu Basin over the last 30 years

Land use change, a result of anthropogenic activities, drives the long-term dynamics of nutrient cycling in watersheds (Poor and McDonnell, 2007; Jacobs et al., 2017; Xie et al., 2017). In this study, we evaluated land use change across the Taihu Basin from 1980 to 2010 with ArcGIS 10.1 (ESRI Corporation). We obtained the 1:100000 land use maps in 1980 and in 2010 from the Institute of Geographic Sciences and Natural Resources Research of the Chinese Academy of Sciences. We found that the land use types had changed significantly from 1980 to 2010. Paddy fields, the main land use, decreased from 59% to 44%, and dry land decreased from 5% to 4%. The changes of those two land types implied that lots of cultivated land used for other purposes. Urban area, another major land use type, increased from 10% to 25%, mostly at the expense of cultivated land. The water area increased slightly from 12% to 14%, and the forest area, at 13%, remained unchanged (Fig. 2). These spatial

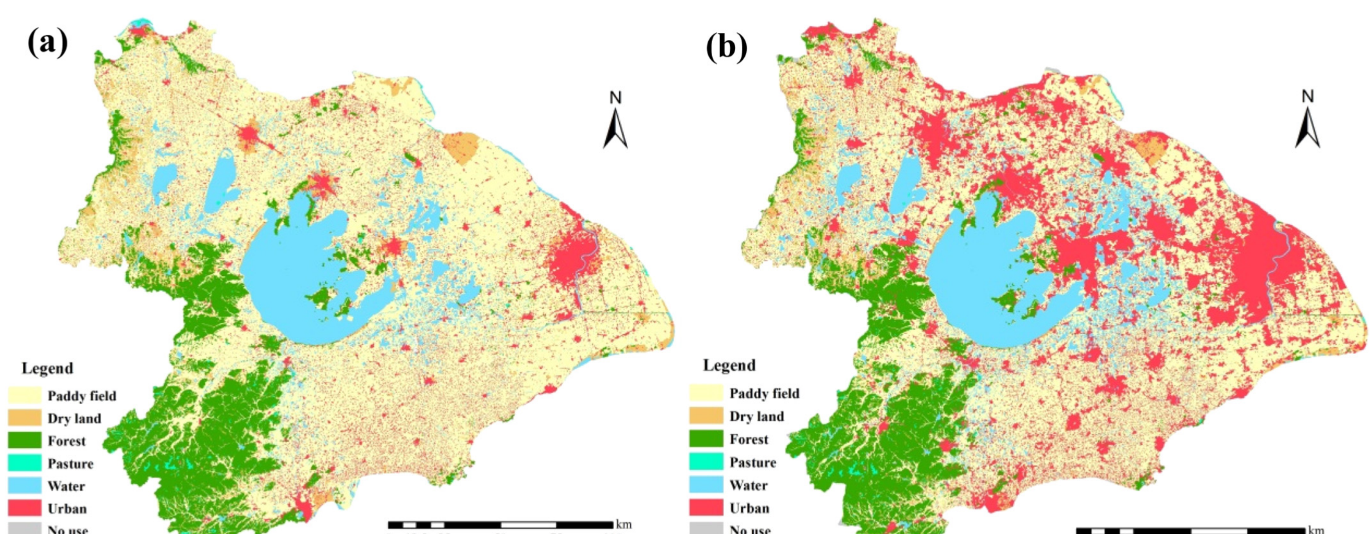

Fig. 2. Land-use in the Taihu Basin in (a) 1980 and (b) 2010. The land-use types are divided into seven categories: paddy field, dry land, forest, pasture, water, urban, and unused land.

and temporal variations in land use formed the basis of our assessment of the N inputs and exports in the Taihu Basin.

2.3. Estimation of the net anthropogenic nitrogen inputs

We calculated the NANI across the Taihu Basin using county-level statistical data in 1980 and in 2010 of Jiangsu, Zhejiang, and Shanghai. The NANI were assumed to be the sum of four N components, namely atmospheric N deposition (Ndep), fertilizer N (Nfer), agricultural N-fixation (Nfix), and net imports of N in food and animal feed (Nim) (Howarth et al., 2012). All four N components are closely related to the N balance in the basin and have direct or indirect impacts on water quality. For instance, atmospheric N is not only deposited directly onto surface water, but also affects soil N dynamics and losses of N to both surface water and groundwater. Fertilizer N that is applied to land in both mineral and organic forms can be washed off by rain or irrigation water. The N fixed by leguminous crops can be released from root systems by microbial decomposition. Finally, the N in food for humans and animal feeds imported to the watershed, exported as waste excreted, has a huge influence on the N balance of the whole system (Swaney et al., 2012).

2.3.1. Atmospheric N deposition (Ndep)

Atmospheric N deposition is a major input of nitrogen (Hobbs et al., 2016) that has increased all over the world in recent years because of intense anthropogenic activities (Duce et al., 2008; Liu et al., 2017). We only calculated oxidized N (NO_x) deposition for Ndep because most ammonium N (NHx) was derived from the emission in the same basin due to the instability of NHx in atmosphere. Thus, we did not consider it as new input to the basin (Howarth et al., 1996). Information about the amount of atmospheric N deposition in the Taihu Basin was acquired from a previous study (Ti et al., 2011; Han et al., 2014; Song et al., 2005).

2.3.2. Fertilizer N applications (Nfer)

Information about the amount of fertilizer applied was obtained from local agricultural statistical almanacs in 1980 and in 2010. We conducted face-to-face interviews with agricultural service departments, village committees, farmers and agricultural product sales personnel in Yixing, Jiangsu province, to obtain information about fertilizer use in the basin. We obtained a total of 76 valid questionnaires. Our survey included questions about the area of farmland, crop species, rotation patterns, and methods and rates of fertilizer application. We found that the N component of compound fertilizer was 15% on average.

2.3.3. Agricultural N-fixation (Nfix)

Fixation of atmospheric N by N-fixing plants represents another supply of N to the basin. Microorganisms in the roots of N-fixing crops transfer the molecular N in the air to ammonia through a series of biochemical processes. There are two types of nitrogen fixation, free-living N-fixation and symbiotic N-fixation. Because symbiotic N-fixation generally dominates, and free-living N fixation is very limited, we only considered symbiotic N-fixation in this study. We used the N-fixation rates of the main N-fixing crops, peanuts (8000 N km^{-2} yr^{-1}) and soybeans (10,000 kg N km^{-2} yr^{-1}), in the Taihu Basin from a previous study (Smil, 1999). Then we estimated the agricultural N-fixation by multiplying the N-fixation rates by the corresponding crop areas using an area-based method (Hong et al., 2013).

2.3.4. Net food and animal feed imports (Nim)

We calculated the net food and animal feed imports to the Taihu Basin by subtracting the consumed N by humans and livestock from the produced N. The consumed N was calculated by multiplying the number of humans and animals with the amount of food-N consumed per capita. We used N consumption rates of 3.95 and 3.71 kg N $capita^{-1}$-yr^{-1} for rural and urban residents in 2010, respectively, and of 16.68, 66.75, 6.85, 0.60 kg N $capita^{-1}$ yr^{-1} for swine, cow, sheep, chicken respectively (Wu, 2005; Zhai et al., 2005) Food N production was estimated from eight main crops, all fruits, vegetables and animal husbandry. The population, animal, and crop production data were collected from Statistical Reports published by Jiangsu Province, Zhejiang Province, and the Shanghai Municipality. We used the N content of crops and animals (Supplementary Table 1) published by the China Food Composition (Yang et al., 2010). Han et al. (2014) found that human N consumption increased by 16% over the 30 years (Han et al., 2014), according to this rate we calculated the N consumption in 1980 based on in 2010. We calculated the net food and feed imports with Eq. (1) (Gao Wei, 2014), as follows:

$$\mathrm{Nim} = \mathrm{N_{hc}} + \mathrm{N_{lc}} - \mathrm{N_{lp}} - \mathrm{N_{cp}} \tag{1}$$

where Nim represents the net imports of food and feed, N_{hc} and N_{lc} are the human and livestock N consumption, respectively, and N_{lp} and N_{cp} are the N contents of livestock and crop production, respectively, in the basin.

2.4. Estimation of N exports with the Export Coefficient Model (ECM)

The Export Coefficient Model is a mathematical weighted equation that can be used to calculate the annual pollution load, and to estimate the pollutant load exported from different sources to water bodies (Shrestha et al., 2008; Lu et al., 2013). The ECM can represent the interactions among land use types, pollutants, livestock, and N exports load. The basic expression of the ECM is as follows:

$$L = \sum_{i=1}^{m} \mathrm{EiAi}$$

where L is the amount of N exports, Ei is the export coefficient for each pollution source, and the export coefficients (Supplementary Table 2) for different pollution sources in the Taihu Basin were collected from previous studies. Ai is the area of land use or the number of the population or animals for each pollution source, and m is the total number of pollution sources (Johnes, 1996). The areas covered by the different land use types in the 45 counties in 1980 and in 2010 were calculated based on the land use map provided by the Institute of Geographic Sciences and Natural Resources Research of the Chinese Academy of Sciences. The population, livestock and poultry breeding data for each county were collected from local statistical yearbooks.

We calibrated the model with the observed TN concentrations and flow data (Supplementary Table 3) (Lian et al., 2017a; Lian et al., 2017b) and found that the export coefficient model was a simple and reliable way to evaluate the N loads in the Taihu Basin. We calculated the pollutants exported from crop production source (CPS), livestock source (LS), rural life source (RLS), urban life source (ULS), and others sources (OS). We used the export coefficients for the different pollution sources in the Taihu Basin from previous studies (Cai et al., 2004; Liu et al., 2009; Wu et al., 2012; Du Juan et al., 2013; Zhou et al., 2014; Shen et al., 2013). According to the variation of fertilization intensity and consumption of human and livestock, we calculated the N export coefficients in 1980 based on in 2010.

2.5. Uncertainty analysis

First, to generate reliable results from models, the statistical data must be accurate. In previous model applications, the accuracy and type of data used by different scholars varied, and including national-, provincial-, municipal-, county-, and even township-level statistics (Han et al., 2014; Swaney et al., 2015; Gao et al., 2016). At these different levels, the total amount of N did not change, but the spatial distribution of N was improved as the accuracy of the data increased. Our estimates were based on county-level data, and could help local governments to implement different N management policies in the various administrative regions. Secondly, the accuracy of the model parameters can also influence the simulation results. The export coefficients of the model must represent the entire basin. We reviewed many previous studies in which the exports from different sources in the Taihu Basin were calculated. Minimum and maximal N load under different value of parameters were shown in (Supplementary Table 5).

3. Results

3.1. Spatial and temporal variations of NANI from 1980 to 2010

Spatial variations of NANI over the study period are shown in Fig. 3. The NANI in the Taihu Basin increased 50% over the 30 years, with greater increases in the eastern plain than in the western hilly region. The NANI of 45 counties in the Taihu Basin ranged from 1860 to 19,884 kg N km^{-2} yr^{-1}, with an average of 6432 kg N km^{-2} yr^{-1} in 1980, while ranged from 2253 to 37,692 kg N km^{-2} yr^{-1}, with an average of 9722 kg N km^{-2} yr^{-1} in 2010.

The composition of NANI changed considerably over the past 30 years. While fertilizer applications were the main source of N inputs throughout, their contributions to the total NANI decreased from 77% in 1980 to 53% in 2010. The overall fertilizer application in 1980 was 180,738 tons, while 179,882 tons in 2010. The total numbers of fertilizer application in those two periods were very close to each other, but it decreased in 2010. In addition, the cultivated land had decreased from 23,259 km^2 to 17,237 km^2. Thus, it can be concluded that the fertilizer application rates per unit area actually increased over the study period. The percentage of food and animal feed N inputs of NANI increased from 11% to 16%, N-fixation by crops increased from 2% to 15%, and N deposition increased from 10% to 16% (Fig. 4). It was previously reported that atmospheric N deposition in the Taihu Basin increased from 677 to 1363 kg N km^{-2} yr^{-1} over the 30 years from 1980 to 2010 (Han et al., 2014).

3.2. Spatial and temporal variations of N exports from 1980 to 2010

N exports from the eastern plain area were higher than those from the western hilly region (Fig. 5). The N exports from the 45 counties in Taihu Basin ranged from 1042 to 5750 kg N km^{-2} yr^{-1} in 1980, with an average of 3170 kg N km^{-2} yr^{-1}. While in 2010, the N exports ranged from 1235 to 201,245 kg N km^{-2} yr^{-1}, with an average of 4582 kg N km^{-2} yr^{-1}. N exports were generally high in areas where the population density was high, and were low in the southwest of the basin, where woodland is the main land use types. We found that

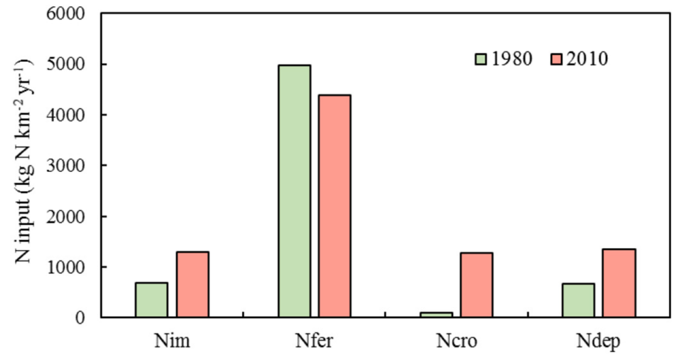

Fig. 4. The four components of NANI in 1980 and 2010. Nim, Nfer, Ncro, and Ndep represent net imports of N in food and animal feeds, fertilizer N applications, crop N-fixation, and atmospheric N deposition, respectively.

the N exports from Wuxi City decreased over the study period, possibly because of the changes in the production structure and improvements in farm management practices.

We calculated the N exports from different sources, including farming, aquaculture, rural life, urban life, and other land use types (Fig. 6) and found that the contributions from the main pollution sources changed considerably between 1980 and 2010. Crop production was the main source of the N exported, and accounted for 40% and 28% of the total N exports in 1980 and 2010, respectively. The N exports from urban life increased from 7% in 1980 to 22% in 2010, while those from rural areas decreased, reflecting the increases with the urbanization.

3.3. The relationship between NANI and N exports

The N exports from the 45 counties were significantly and positively correlated with the NANI in 1980 and 2010 (Fig. 7). The slopes of the fitting equations indicated that, on average, approximately 19% and 38% of the NANI were exported to water bodies in 1980 and 2010, respectively. We also noticed a saturation effect in the N exports relative to the N inputs.

4. Discussion

Over recent decades, N inputs and exports have changed considerably worldwide as the intensity of anthropogenic activities has increased (Boyer et al., 2002; Han et al., 2014; Gao et al., 2015; Swaney et al., 2015). During our study period, we found that the NANI in the

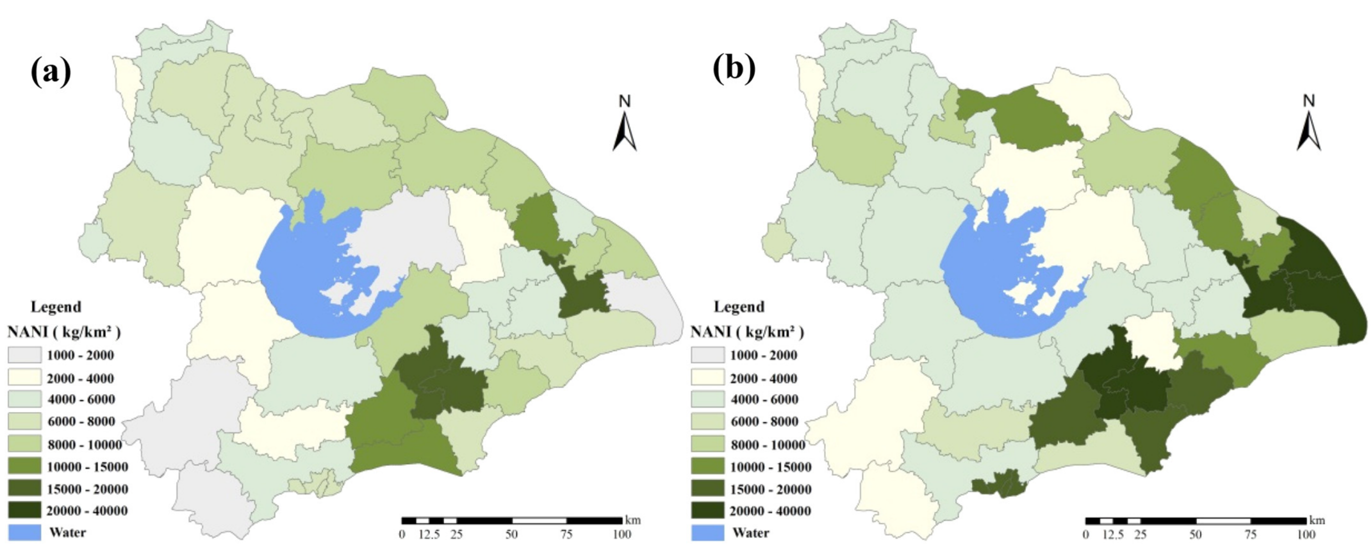

Fig. 3. Spatial distribution of NANI in the Taihu Basin at the county level in (a) 1980 and (b) 2010.

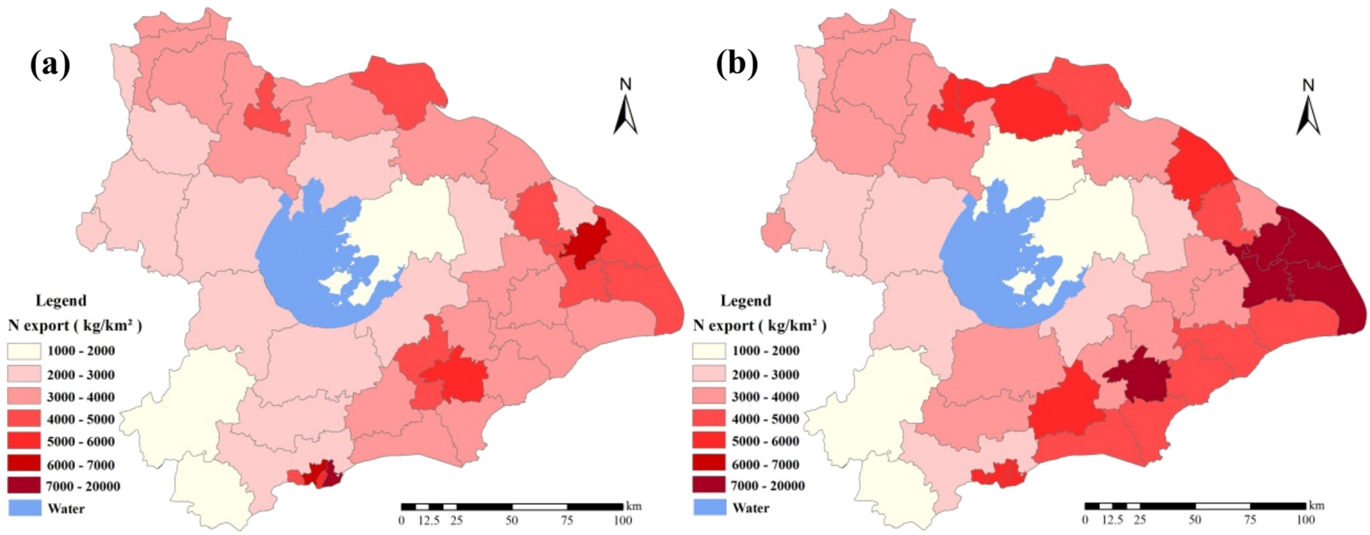

Fig. 5. Spatial distribution of N exports to the Taihu Basin at the county level in (a) 1980 and (b) 2010.

Taihu Basin increased from 6432 to 9722 kg N km^{-2} yr^{-1}. Comparison with similar studies shows that the NANI in the Taihu Basin in 2010 were 1.9, 5.0 and 2.1 times higher than the same averages for China, the USA and India, respectively (Boyer et al., 2002; Han et al., 2014; Swaney et al., 2015). These increases are not unique to the Taihu Basin; for example, from 1980 to 2010, NANI in the Dianchi Basin increased from 4700 to 12,600 kg N km^{-2} yr^{-1} (Gao et al., 2015), and the rate of increase was considerably greater than in the Taihu Basin. The compositions of the NANI for the Taihu and Dianchi basins also varied considerably. In the Taihu Basin, the contribution of Nim to the total N inputs increased from 11% to 16%, Nfix increased from 2% to 15% and Ndep increased from 10% to 16%, however, Nfer decreased from 77% to 53%. Those changes reflected the rapid development of urbanization in the basin and the decreased contribution of agriculture to N inputs. On the other hand, the proportions of Nim and Nfer increased from 1980 to 2010 in the Dianchi Basin, while Nfix and Ndep did not change, as also occurred in the St. Lawrence sub-basin in the Great Lakes Region of North America (Goyette et al., 2016). Large areas of arable land have been converted to construction land in the Taihu Basin because agriculture was no longer economically profitable in rural areas. Over the 30 years, N exports in the Taihu Basin increased from 3170 to 4582 kg N km^{-2} yr^{-1}. The changes in the composition of the N inputs and exports reflected the economic and social development, changes in farming practices, reductions in crop production and the rapid urbanization in the Taihu Basin.

We examined N inputs/exports budgets with the N export ratio (Huang et al., 2016) and found that 38% of the N inputs were exported to water bodies in 2010, which was double the proportion exported in 1980 and was also higher than the N export ratio estimates of 20%–25% reported elsewhere (Boyer et al., 2002; Goyette et al., 2016; Hobbie et al., 2017). Compared with retention of approximately 75% in other watersheds (Groffman et al., 2004), only 63% of the N inputs to the Taihu Basin was retained within the basin. The variation in the export ratio between these different catchments indicated N saturation and showed that the N surplus in the Taihu Basin was so heavy that the excess N could not be retained. De Girolamo et al. (2017) found that excessive N inputs could induce saturation (De Girolamo et al., 2017). In general, the lower the N inputs, the greater the amount of N retained in the watershed (Gao et al., 2015). When N inputs exceed the storage capacity of the watershed ecosystem, the N capacity becomes saturated and the surplus N is exported. Because of the increases in anthropogenic N inputs over the last three decades, the proportion of the N exports in the Taihu Basin increased by 19%. Hong et al. (2017) found that the relationship between net N inputs and riverine nutrient fluxes did not vary significantly between 2000 and 2010 (Hong et al., 2017) and demonstrated that N export ratios would not change in undisturbed basins. There is the evidence showed that N export ratios were generally higher in highly-disturbed watersheds than in less-disturbed watersheds (Huang et al., 2016), and this suggested that the

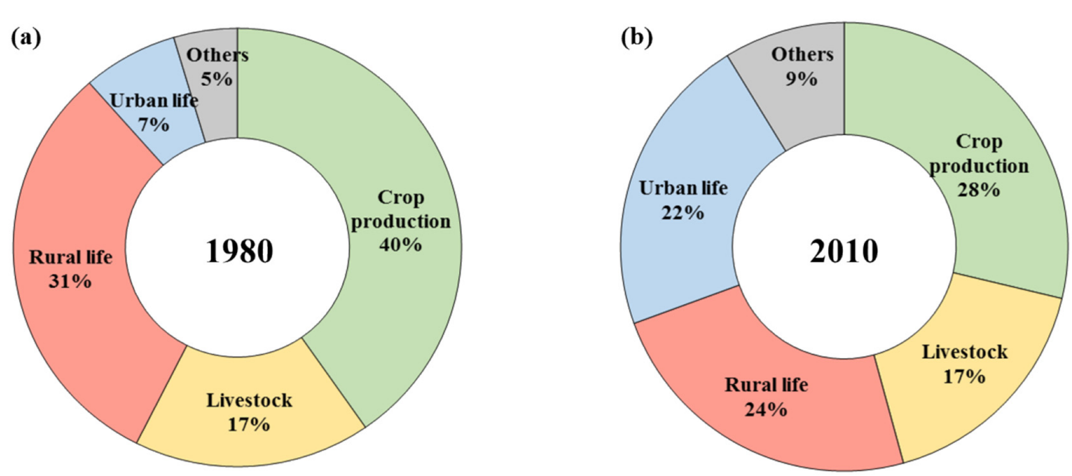

Fig. 6. The contribution of different N sources to nitrogen export in 1980 and 2010.

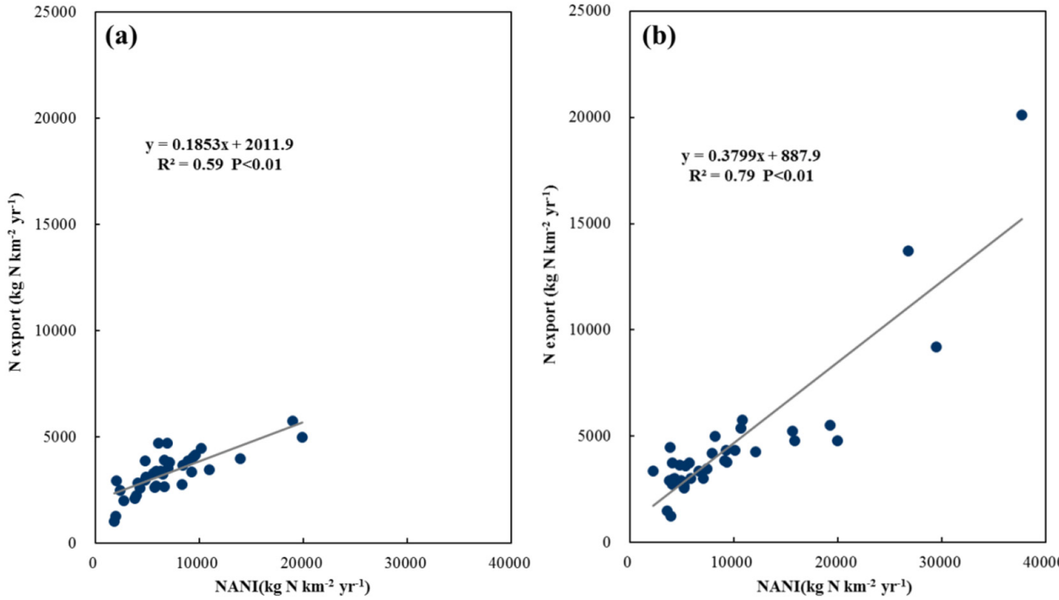

Fig. 7. Relationships between N exports and net anthropogenic N inputs (NANI) from counties in the Taihu Basin in (a) 1980 and (b) 2010. Approximately 19% of NANI were exported in 1980, while 38% were exported in 2010.

N-cycling in the Taihu Basin was disturbed by intense anthropogenic activities.

To determine how human activities influenced the N balance in the Taihu Basin, we compared the N cycling in 1980 and in 2010. The levels of social and economic development, land use change and population density were the main impact factors on N exports to water environment in the Taihu Basin (Fig. 8). We found that NANI and N exports were significantly correlated with urban area (%), urban population (%), population density, and the GDP (Supplementary Table 4). Also, the hotpots of N inputs and exports (Figs. 3, 4) were the counties with heavy population density and high levels of urbanization. While other researchers reported a strong linear relationship between NANI and the proportion of cropland (Zhang et al., 2016), and our study showed that NANI, N exports, and the proportion of cultivated land in the Taihu Basin were not significantly correlated. Therefore, it demonstrated that the changes in the N budgets in the Taihu Basin were mainly driven by urbanization and economic growth.

When we made reasonable estimates of various components of the N cycle, we could improve our estimates of the pollution in the Taihu Basin by studying N cycling at the macroscopic scale. We should also carry out a more detailed assessment of the potential pollution risks to determine how human activities influence the N cycle. The residence time of N has an important role in plain river networks. Because of the flat terrain, the slope of the river is low, and N moves slowly from land to water. As the retention time increases, the amount of N converted into a gaseous form and volatilized during denitrification will also increase, thereby reducing the amount of N exported to freshwater and the potential for eutrophication. We identified the main inputs and exports of N in the basin, which can be used as a basis for controlling the sources and transport of N in the basin. However, to control N in the

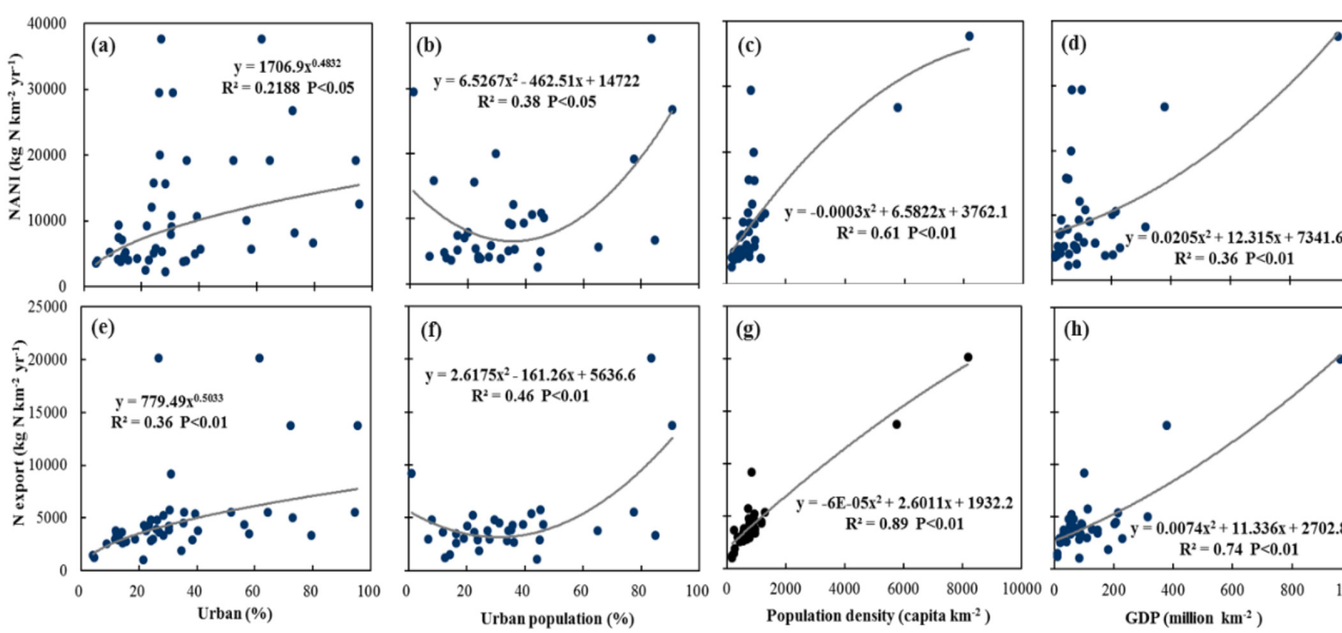

Fig. 8. Relationships between NANI and N export for several human activity indexes in 1980 (a, b, c, d) and 2010 (e, f, g, h). Those indexes include Urban (%), which means the percentage of urban area to the basin area; the urban population (%) is the percentage of urban population to the total population; population density; GDP.

future, strategies should consider N retention and how to control N exports by using measures such as ditches, swamps, and buffers to reduce N pollution.

Nitrogen loads in this study were calculated based on two empirical models. The uncertainty discussed in this study is mainly attributed from the value of parameters due to the relatively limited experimental data (specifically, parameter uncertainty). Thus, parameter uncertainty was considered and ranges of results were examined accordingly. In this study, uncertainty from parameters could be effectively reduced by acquiring long-term and abundant measurement data.

5. Conclusion

In this study, we highlighted the spatial and temporal variations in N inputs and exports in the Taihu Basin from 1980 to 2010. The NANI method and the ECM were first integrated to assess N load in a basin. We found that net N inputs to the basin increased from 6432 to 9722 kg N km^{-2} yr^{-1} and N exports increased from 3170 to 4582 kg N km^{-2} yr^{-1} over the study period. Depredations of N balance (1980–2010) were investigated in the Taihu Basin, and anthropogenic activities are the primary contributors of fast-growing N loads. Urbanization, economic and population growth are key factors of spatial-temporal changes.

Acknowledgements

This study was supported by funding from the Special Fund for Agroscientific Research in the Public Interest (Grant No.: 201303089), the National Natural Science Foundation of China (Grant No.: 31572208), and the Newton Fund (Grant Ref: BB/N013484/1). And acknowledgement for the data support from "Lake-Watershed Science Data Center, National Earth System Science Data Sharing Infrastructure, National Science & Technology Infrastructure of China. (http://lake.geodata.cn)".

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.06.354.

References

Boyer, E.W., Goodale, C.L., Jaworsk, N.A., Howarth, R.W., 2002. Anthropogenic nitrogen sources and relationships to riverine nitrogen export in the northeastern USA. Biogeochemistry 57, 137–169.

Bureau of Taihu Lake Basin, Ministry of Water Resources, 2010. The health status report of Taihu Lake. http://www.tba.gov.cn//tba/content/TBA/lygb/thjkzkbg/0000000000000932.html, Accessed date: 19 March 2018.

Cai, M., Li, F., Zhuang, Y., Wang, Q., 2004. Application of modified export coefficient method in polluting load estimation of non-point source pollution. J. Hydraul. Eng. 0, 40–45.

Carpenter, S.R., Caraco, N.F., Correll, D.L., Howarth, R.W., Sharpley, A.N., Smith, V.H., 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecol. Appl. 8, 559–568.

Chen, Y., Gao, W., Wang, D., Liu, Y., Wu, Y., Guo, H., 2016. Net anthropogenic nitrogen inputs (NANI) and riverine response in water shortage region: a case study of Haihe River watershed. Acta Sci. Circumst. 36, 3600–3606.

Chen, D., Hu, M., Guo, Y., Dahlgren, R.A., 2016. Modeling forest/agricultural and residential nitrogen budgets and riverine export dynamics in catchments with contrasting anthropogenic impacts in eastern China between 1980–2010. Agric. Ecosyst. Environ. 221, 145–155.

De Girolamo, A.M., Balestrini, R., D'Ambrosio, E., Pappagallo, G., Soana, E., Lo Porto, A., 2017. Antropogenic input of nitrogen and riverine export from a Mediterranean catchment. The Celone, a temporary river case study. Agric. Water Manag. 187, 190–199.

Du Juan, Li, H., Li, J., 2013. Analysis on export coefficients based on measured data and study on the sources of non-point load for Fenghe River Watershed in Shaanxi Province,China. Agric. Agro-Environ. Sci. 32, 827–837.

Duce, R.A., LaRoche, J., Altieri, K., Arrigo, K.R., Baker, A.R., Capone, D.G., Cornell, S., Dentener, F., Galloway, J., Ganeshram, R.S., Geider, R.J., Jickells, T., Kuypers, M.M., Langlois, R., Liss, P.S., Liu, S.M., Middelburg, J.J., Moore, C.M., Nickovic, S., Oschlies, A., Pedersen, T., Prospero, J., Schlitzer, R., Seitzinger, S., Sorensen, L.L., Uematsu, M., Ulloa, O., Voss, M., Ward, B., Zamora, L., 2008. Impacts of atmospheric anthropogenic nitrogen on the open ocean. Science 320, 893–897.

Galloway, J.N., Aber, J.D., Erisman, J.W., Seitzinger, S.P., Howarth, R.W., Cowling, E.B., Cosby, B.J., 2003. The nitrogen cascade. Bioscience 53, 341–356.

Gao Wei, G.H.H.X., 2014. Evaluating city-scale net anthropogenic nitrogen input (NANI) in mainland China. Acta Sci. Nat. Univ. Pekin. 951–959.

Gao, W., Howarth, R.W., Swaney, D.P., Hong, B., Guo, H.C., 2015. Enhanced N input to Lake Dianchi Basin from 1980 to 2010: drivers and consequences. Sci. Total Environ. 505, 376–384.

Gao, W., Gao, B., Yan, C., Liu, Y., 2016. Evolution of anthropogenic nitrogen and phosphorus inputs to Lake Poyang Basin and its' effect on water quality of lake. Acta Sci. Circumst. 36, 3137–3145.

Goyette, J., Bennett, E.M., Howarth, R.W., Maranger, R., 2016. Changes in anthropogenic nitrogen and phosphorus inputs to the St. Lawrence sub-basin over 110 years and impacts on riverine export. Glob. Biogeochem. Cycles 30, 1000–1014.

Groffman, P.M., Law, N.L., Belt, K.T., Band, L.E., Fisher, G.T., 2004. Nitrogen fluxes and retention in urban watershed ecosystems. Ecosystems 7, 393–403.

Han, Y., Fan, Y., Yang, P., Wang, X., Wang, Y., Tian, J., Xu, L., Wang, C., 2014. Net anthropogenic nitrogen inputs (NANI) index application in Mainland China. Geoderma 213, 87–94.

Hobbie, S.E., Finlay, J.C., Janke, B.D., Nidzgorski, D.A., Millet, D.B., Baker, L.A., 2017. Contrasting nitrogen and phosphorus budgets in urban watersheds and implications for managing urban water pollution. Proc. Natl. Acad. Sci. U. S. A. 114, E4116.

Hobbs, W.O., Lafrancois, B.M., Stottlemyer, R., Toczydlowski, D., Engstrom, D.R., Edlund, M.B., Almendinger, J.E., Strock, K.E., VanderMeulen, D., Elias, J.E., Saros, J.E., 2016. Nitrogen deposition to lakes in national parks of the western Great Lakes region: isotopic signatures, watershed retention, and algal shifts. Glob. Biogeochem. Cycles 30, 514–533.

Hollinger, E., Cornish, P.S., Baginska, B., Mann, R., Kuczera, G., 2001. Farm-scale stormwater losses of sediment and nutrients from a market garden near Sydney, Australia. Agric. Water Manag. 47, 227–241.

Hong, B., Swaney, D.P., Howarth, R.W., 2013. Estimating net anthropogenic nitrogen inputs to US watersheds: comparison of methodologies. Environ. Sci. Technol. 47, 5199–5207.

Hong, B., Swaney, D.P., McCrackin, M., Svanback, A., Humborg, C., Gustafsson, B., Yershova, A., Pakhomau, A., 2017. Advances in NANI and NAPI accounting for the Baltic drainage basin: spatial and temporal trends and relationships to watershed TN and TP fluxes. Biogeochemistry 133, 245–261.

Howarth, R.W., Billen, G., Swaney, D., Townsend, A., Jaworski, N., Lajtha, K., Downing, J.A., Elmgren, R., Caraco, N., Jordan, T., Berendse, F., Freney, J., Kudeyarov, V., Murdoch, P., Zhu, Z.L., 1996. Regional nitrogen budgets and riverine N&P fluxes for the drainages to the North Atlantic Ocean: natural and human influences. Biogeochemistry 35, 75–139.

Howarth, R.W., Swaney, D.P., Boyer, E.W., Marino, R., Jaworski, N., Goodale, C., 2006. The influence of climate on average nitrogen export from large watersheds in the Northeastern United States. Biogeochemistry 79, 163–186.

Howarth, R., Swaney, D., Billen, G., Garnier, J., Hong, B., Humborg, C., Johnes, P., Morth, C., Marino, R., 2012. Nitrogen fluxes from the landscape are controlled by net anthropogenic nitrogen inputs and by climate. Front. Ecol. Environ. 10, 37–43.

Huang, J., Lee, T., Lin, T., Hein, T., Lee, L., Shih, Y., Kao, S., Shiah, F., Lin, N., 2016. Effects of different N sources on riverine DIN export and retention in a subtropical high-standing island, Taiwan. Biogeosciences 13, 1787–1800.

Jacobs, S.R., Breuer, L., Butterbach-Bahl, K., Pelster, D.E., Rufino, M.C., 2017. Land use affects total dissolved nitrogen and nitrate concentrations in tropical montane streams in Kenya. Sci. Total Environ. 603, 519–532.

Jian Xinhua, H.K., 2010. Empirical analysis and forecast of the level and speed of urbanization in China. Econ. Res. J. 28–39.

Johnes, P.J., 1996. Evaluation and management of the impact of land use change on the nitrogen and phosphorus load delivered to surface waters: the export coefficient modelling approach. J. Hydrol. 183, 323–349.

Lai, Z., Li, S., Lv, G., Pan, Z., Fei, G., 2016. Watershed delineation using hydrographic features and a DEM in plain river network region. Hydrol. Process. 30, 276–288.

Li, S., Zhang, L., Du, Y., Liu, H., Zhuang, Y., Liu, S., 2016. Evaluating phosphorus loss for watershed management: integrating a weighting scheme of watershed heterogeneity into export coefficient model. Environ. Model. Assess. 21, 657–668.

Lian, H., Liu, H., Li, X., Song, T., Lei, Q., Ren, T., Wu, S., Li, Y., 2017a. Analysis of spatial variability of water quality and pollution sources in Lihe River Watershed,Taihu Lake Basin. Environ. Sci. 38, 3657–3665.

Lian, H., Liu, H., Li, X., Song, T., Liu, S., Lei, Q., Ren, T., Wu, S., Li, Y., 2017b. Characteristics of nitrogen variation and its response to rainfall: a case study in Wuxi Port at Taihu Lake Basin. Environ. Sci. 38, 5047–5055.

Liu, R., Yang, Z., Shen, Z., Yu, S.L., Ding, X., Wu, X., Liu, F., 2009. Estimating nonpoint source pollution in the upper Yangtze River using the export coefficient model, remote sensing, and geographical information system. J. Hydraul. Eng. 135, 698–704.

Liu, L., Zhang, X., Zhang, Y., Xu, W., Liu, X., Zhang, X., Feng, J., Chen, X., Zhang, Y., Lu, X., Wang, S., Zhang, W., Zhao, L., 2017. Dry particulate nitrate deposition in China. Environ. Sci. Technol. 51, 5572–5581.

Lu, S., Yuan, Y., Jin, X., Jiao, W., Wu, Y., Ren, D., Zhou, Y., Chen, L., 2012. Speciation distribution of nitrogen in sediments of 7 rivers around Taihu Lake. Chin. J. Environ. Sci. 33, 1497–1502.

Lu, J., Gong, D., Shen, Y., Liu, M., Chen, D., 2013. An inversed Bayesian modeling approach for estimating nitrogen export coefficients and uncertainty assessment in an agricultural watershed in eastern China. Agric. Water Manag. 116, 79–88.

Ma Ronghua, Y.G.D.H., 2011. The quantity, area and spatial distribution of lakes in China. Sci. China Earth Sci. 394–401.

McIsaac, G.F., David, M.B., Gertner, G.Z., Goolsby, D.A., 2001. Eutrophication - nitrate flux in the Mississippi river. Nature 414, 166–167.

Poor, C.J., McDonnell, J.J., 2007. The effects of land use on stream nitrate dynamics. J. Hydrol. 332, 54–68.
Qin, B., Xu, P., Wu, Q., Luo, L., Zhang, Y., 2007. Environmental issues of Lake Taihu, China. Hydrobiologia 581, 3–14.
Shen, M., Su, B., Huang, N., Yang, W., 2013. Rural domestic pollution around Taihu Lake and estimation of loss rate. J. Beijing Normal Univ. Nat. Sci. 49, 261–265.
Shih, Y., Lee, T., Huang, J., Kao, S., Chang, F., 2016. Apportioning riverine DIN load to export coefficients of land uses in an urbanized watershed. Sci. Total Environ. 560, 1–11.
Shrestha, S., Kazama, F., Newham, L.T.H., 2008. A framework for estimating pollutant export coefficients from long-term in-stream water quality monitoring data. Environ. Model. Softw. 23, 182–194.
Smil, V., 1999. Nitrogen in crop production: an account of global flows. Glob. Biogeochem. Cycles 13, 647–662.
Song, Y., Qin, B., Yang, L., Hu, W., Luo, L., 2005. Primary estimation of atmospheric wet deposition of nitrogen to aquatic ecosystem of Lake Taihu. Sci. Limnol. Sin. 17, 226–230.
Swaney, D.P., Hong, B., Ti, C., Howarth, R.W., Humborg, C., 2012. Net anthropogenic nitrogen inputs to watersheds and riverine N export to coastal waters: a brief overview. Curr. Opin. Environ. Sustain. 4, 203–211.
Swaney, D.P., Hong, B., Selvam, A.P., Howarth, R.W., Ramesh, R., Purvaja, R., 2015. Net anthropogenic nitrogen inputs and nitrogen fluxes from Indian watersheds: an initial assessment. J. Mar. Syst. 141, 45–58.
Ti, C., Xia, Y., Pan, J., Gu, G., Yan, X., 2011. Nitrogen budget and surface water nitrogen load in Changshu: a case study in the Taihu Lake region of China. Nutr. Cycl. Agroecosyst. 91, 55–66.
Wan, R., Cai, S., Li, H., Yang, G., Li, Z., Nie, X., 2014. Inferring land use and land cover impact on stream water quality using a Bayesian hierarchical modeling approach in the Xitiaoxi River Watershed, China. J. Environ. Manag. 133, 1–11.
Wang, S., Shan, J., Xia, Y., Tang, Q., Xia, L., Lin, J., Yan, X., 2017. Different effects of biochar and a nitrification inhibitor application on paddy soil denitrification: a field experiment over two consecutive rice-growing seasons. Sci. Total Environ. 593, 347–356.
Worrall, F., Burt, T.P., Howden, N.J.K., Whelan, M.J., 2012. The fluvial flux of nitrate from the UK terrestrial biosphere - an estimate of national-scale in-stream nitrate loss using an export coefficient model. J. Hydrol. 414, 31–39.
Wu, S., 2005. The Spatial and Temporal Change of Nitrogen and Phosphorus Produced by Livestock and Poultry & Their Effects on Agricultural Non-point Pollution in China. The Chinese Academy of Agricultural Science.
Wu, Y., Li, W., Yu, Y., Li, R., Long, B., Shi, J., 2012. Non-point source pollution loadings in Xitiaoxi Watershed of Anji County,Zhejiang Province,China. J. Agro-Environ. Sci. 31, 1976–1985.
Xia, Y., Ti, C., She, D., Yan, X., 2016. Linking river nutrient concentrations to land use and rainfall in a paddy agriculture-urban area gradient watershed in southeast China. Sci. Total Environ. 566, 1094–1105.
Xie, C., Huang, X., Mu, H., Yin, W., 2017. Impacts of land-use changes on the lakes across the Yangtze floodplain in China. Environ. Sci. Technol. 51, 3669–3677.
Yang, Y., Wang, G., Pan, X., 2010. China Food Composition. Peking University Medical Press, Beijing.
Zhai, F., He, Y., Wang, Z., Yu, W., Hu, Y., Yang, X., 2005. The status and trends of dietary nutrients intake of Chinese population. Acta Nutrimenta Sin. 27, 181–184.
Zhang, W., Li, X., Su, J., 2014. Responses of riverine nitrogen export to net anthropogenic nitrogen inputs: a review. Chin. J. Appl. Ecol. 25, 272–278.
Zhang, W., Su, J., Xinzhong, Du, Li, X., 2015. Net anthropogenic nitrogen input to Huaihe River Basin,China during 1990–2010. Chin. J. Appl. Ecol. 26, 1831–1839.
Zhang, W., Li, X., Swaney, D.P., Du, X., 2016. Does food demand and rapid urbanization growth accelerate regional nitrogen inputs? J. Clean. Prod. 112, 1401–1409.
Zhou, Y., Wang, H., Yu, H., Wang, Z., 2014. Estimation of nutrient export loads in Taihu lake watershed based on the export coefficient model. Acta Agric. Univ. Jiangxiensis 36, 678–683.