A framework to quantify riverine dissolved inorganic nitrogen exports under changing land use pattern and hydrologic regime

Zhenyu Zhang[1], Jr-Chuan Huang[2], Jinliang Huang[*1]

[1]Fujian Key Laboratory of Coastal Pollution Control, Xiamen University, 361102, Xiamen, China

[2]Department of Geography, National Taiwan University, Taipei, Taiwan

***Corresponding Author**

J Huang (jlhuang@xmu.edu.cn)

Abstract:

Riverine dissolved inorganic nitrogen (DIN), when elevated by human activities (e.g., land-use change), can accelerate the nitrogen cycle and downstream dispersal. However, estimating DIN export coefficients for individual land-use types can be complex due to mosaic land-use patterns and interactions between fertilizers and hydrological processes. We propose a framework that integrates an empirical model, a moving-window method with an elasticity method to quantify seasonal DIN export coefficients for each land use in the Shixi Creek catchment, southeast China. Our model showed good agreement with field observations according to root mean square error and a normalized objective function. The DIN export coefficients of farmland and forest were the highest (9.16 mg/L) and lowest (2.91 mg/L), respectively, resulting in DIN exports for farmland and forest of 1,951 kg km^{-2} yr^{-1} and 619 kg km^{-2} yr^{-1}, respectively. Urbanization was a dominant factor influencing DIN export represented by the export coefficient of built-up areas with the highest elasticity and highest

uncertainty. This study can shed light on how to improve riverine N management in a catchment by considering the interactive effects of climate and land use changes.

Keywords: Dissolved inorganic nitrogen; elasticity; export coefficient; land-use change.

1. Introduction

Land-use change has increased the release of reactive nitrogen (N) in the environment and accelerated the N cycle in recent decades, becoming an issue of global significance (Galloway et al., 2008; Mclauchlan et al., 2013). Land-use patterns can predict riverine N export (Huang et al., 2015; Zhou et al., 2016;) and many watershed models including SPARROW (SPAtially Referenced Regression On Watershed attributes; Zhou et al., 2018), SWAT (Soil and Water Assessment Tool; Huang et al., 2013a), HSPF (Hydrological Simulation Program – FORTRAN; Zhang et al., 2019) and the N-runoff model (Mander et al., 2000; Parn et al., 2018) account for land use in their estimates of riverine N export. The performance of these models relies on accurate observed N export and export coefficients for different land-use types (Huang et al., 2012; Shih et al., 2016), hence estimating the N export coefficients of different land uses is critical for watershed modeling and subsequent watershed management.

Riverine N export is strongly controlled by land-use patterns, but few studies have quantified the impacts of individual land-use types. Huang et al. (2012a) applied an empirical model to inversely estimate the DIN (dissolved inorganic nitrogen, including NO^{2-}, NO^{3-}, and NH_4^+) export coefficient of each land use from riverine DIN export. Shih et al. (2016) considered the sources of DIN (point and non-point) with runoff variation into the modification and applied their model to the Taiwan River with good predictive accuracy for river DIN export.

N export from landscapes to watersheds is a complex and nonlinear process influenced by multiple factors, including intra-annual variation in rainfall and associated biogeochemical processes (Lee et al., 2016; Zhou et al., 2017; Zhang et al., 2019). Although export coefficients can quantify N exports for each land use, the relationship between runoff and N loads varies with time and is often poorly accounted for (Tomer et al., 2003; Zhang and Schilling, 2005; de Girolamo et al., 2019). For example, storms can increase N export due to excessive water in the soil and decreasing biogeochemical transformation, especially during wet years (Greaver et al., 2016; Li et al., 2019a; Ervinia et al., 2019).

Some studies stated that riverine N may be amplified by the interaction between increasing human-impacted land use with intensified precipitation (Kaushal et al., 2014; Huang et al., 2018). However, few studies reported how to quantify DIN export coefficients for individual land-use types, which may be likely due to the fact that mosaic land-use patterns and interactions between fertilizers and hydrological processes exist in watersheds. More attempts need to be made to estimating seasonal DIN export coefficients for each land use in Southeast Asia, Southeast China, particularly Southeast China, since this area is a hotspot of global DIN export associated with rapid urbanization and changing climate variability (Chen et al., 2015; Shih et al., 2016; Huang et al., 2018). The emissions of N and export of DIN in Southeast China is expected to be very high which may be controlled by intensive land use change and rich precipitation. Besides, it remains challenging to evaluate N export within a small creek with sparse data, which is a common situation in China (Zhang et al., 2020).

In this study, we developed a framework to quantify riverine dissolved inorganic nitrogen exports under changing land use pattern and hydrologic regime in a small creek watershed, Southeast China. The specific objectives of this study are: to (1) quantify riverine DIN export according to land-use patterns; (2) to assess the impact of hydrological regimes on those export coefficients; and (3) to conduct scenario analysis to test different land management strategies. This study can shed light on how to improve riverine N management in a catchment by considering the interactive effects of climate and land use changes.

2. Material and methods

2.1. Study area

The Shixi Creek catchment is located in the subtropical Asian monsoon climate and has a drainage area of 38.17 km^2 with four tributaries (Fig. 1). Approximately half of the catchment is covered with forest and another third is used as orchards and farmland. Most built-up areas, accounting for ~10% of the drainage area, are located close to the riparian zone of the Shixi (Fig 1). Streamflow from the Shixi is the main water source for domestic, industrial, and agricultural activities for more than 20,000 local residents.

[Insert Fig. 1 here]

2.2. Analytical framework

We devised a framework integrating an empirical model with moving-window and elasticity methods to apportion riverine DIN export to land-use patterns and streamflow regimes using three steps: (1) data processing; (2) model evaluation; and (3) model application (Fig. 2).

[Insert Fig. 2 here]

2.2.1. Data processing

Water samples were collected from 16 sites from March 2017 to February 2019 (Fig. 1).

The samples were kept at 4°C and amounts of nitrate, nitrite, and ammonium were measured using standard methods (SEPAC, 2002; Huang et al., 2018a) within 24 h of collection. To minimize the influence of sediments, we filtered the water immediately. To quantify land use and streamflow for ungauged sampling sites, we used Landsat-8 images from 2017. Land use was classified into six categories: forest, built-up areas, orchards, farmland, bare lands, and water. Four land-use categories were selected for model development (Table 1).

[Insert Table 1 here]

Discharge was simulated for each sampling site using a simplified conception model, which was proposed by Jackson-Blake et al. (2017). Streamflow measures were taken for each sampling site with doppler flow meters (Greyline MantaRay 71915) in February and July 2017 to calibrate and validate the model. Meteorological data (i.e., precipitation and temperature) were obtained from the China Meteorological Administration (http://data.cma.cn/) to simulate the discharge of the Shixi Creek in 2017–2019.

2.2.2. Model evaluation

Riverine DIN load or yield estimation varies with sampling frequency, estimation method, substance characteristics, flow regimes, and watershed characteristics (Ferguson, 1987; Preston et al., 1989; Shih et al., 2016). Previous studies conclude that many methods (e.g., linear interpolation, global mean, and flow weighted) can be used to estimate riverine DIN export, with no single method clearly outperforming others (Huang et al., 2012; Shih et al., 2016). Both the global mean and flow-weighted methods could be applied with our sample size. The global mean method multiplies the average concentration of all samples by the total discharge within the period, hence this method does not account for hydrological responses (Huang et al., 2019). The flow-weighted method was therefore selected to estimate annual riverine DIN export (Eq. 1). This method weighs concentration by discharge, so flux equals annual discharge volume multiplied by flow-weighted DIN concentrations:

$$L = k\frac{\sum_{i=1}^{n} C_i Q_i}{\sum_{i=1}^{n} Q_i} \times Q_t \tag{1}$$

where L is the river DIN load; C_i is the sample concentrations; Q_i is the discharge at sampling time; k is the constant unit conversion factor; and Q_t is the total discharge.

Empirical models, in contrast to physical models, usually require fewer data points for calibration (Delkash et al., 2018). For riverine N export, land-use patterns and relative proportions are important factors. The Pollutant Load Application (PLOAD) model was developed by the US Environmental Protection Agency (EPA) and uses the empirical N yield of each land-use type to estimate N load at the outlet (US EPA, 2001). However, this model may not be applicable to different regional settings. Huang et al. (2012) and Shih et al. (2016) inversed the PLOAD model, where riverine DIN export at the outlet was calculated as the superimposition of different land uses:

$$L_{\mathrm{A}} = \sum_{i=1}^{n} C_i R F_i \tag{2}$$

where L_A is the riverine DIN export normalized by drainage area; F_i is the proportion of land use in the catchment; R is runoff depth; and C_i is the concentration of DIN export for different land uses. This model does not account for complex in-stream processes but can be applied when stream length is short and flow velocity is high (Huang et al., 2012), as was the case in our mountainous catchment.

Both the root mean square error (RMSE) and the normalized objective function (NOF) were used to evaluate model performance by matching the simulation results with field data measured in 2017 (calibration) and 2018 (validation):

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}(Q_{obs} - Q_{sim})^2}{n}} \quad (3)$$

$$NOF = \frac{RMSE}{Q_{ave}} \quad (4)$$

where Q_{obs}, Q_{sim}, Q_{ave}, and n are observed values, simulated values, the average of observed values, and the number of measurements, respectively. Model predictions are acceptable for NOF values from 0.0 to 1.0 (Gikas, 2014). We used Spearman's correlation coefficient (ρ) to characterize relationships between land use and DIN export.

2.2.3. Model application

To identify inter-annual patterns in riverine DIN exports, a moving-window approach was used to account for changing hydrological regimes. The moving-window method requires the specification of a window length and overlap size between sequential windows (Gall et al., 2001; Choi and Beven, 2007). A moving one-year window with a one-month overlap was used to normalize data from March 2017 to February 2019.

Elasticity analysis was used to quantify the impacts of streamflow regimes on DIN export coefficients. Based on previous studies (Sankarasubramanian et al., 2001; Jiang et al., 2014; Ervinia et al., 2019), the annual runoff elasticity of riverine DIN export for each land-use pattern was described as:

$$E = \frac{C - \overline{C}}{R - \overline{R}} \frac{\overline{R}}{\overline{C}} \quad (5)$$

where $\overline{C}$ and $\overline{R}$ are the means of the DIN export coefficients and runoff depths, respectively, and C and R are the DIN export coefficients and runoff depths at any given time. The median of the value was used to estimate overall elasticity (Jiang et al., 2014). After setting up the model, the baseline riverine DIN export for the catchment was estimated using 2017 land use with different streamflow regimes. These baseline output values were compared to outputs from land-use policy scenarios. We used two land-use policy scenarios: (1) a certain proportion of forest is converted to agricultural land, and (2) a certain proportion of forest is converted to built-up land. We assumed that the proportions of agricultural sub-classes would remain unchanged, with a farmland to orchard ratio of 1:2.5.

3. Results

3.1 Linkage between land use and DIN export using empirical model

The distinct linkage between DIN concentration and land use pattern in this catchment show necessity of determination of export coefficient for individual land. Observed DIN concentrations were positively correlated with the prevalence of orchards (ρ = 0.62; Fig. S1d) and negatively correlated with the prevalence of forests (ρ = −0.63; Fig. S1a). DIN export coefficients for each land use were estimated with Eq. 2. based on 2017 riverine DIN export and runoff depth data, with 2018 data used for validation. DIN export coefficients for forests, built-up areas, orchards, and farmland were 2.91 mg/L, 3.91 mg/L, 3.7 mg/L, and 9.16 mg/L, respectively (Table 2).

[Insert Table 2 here]

The RMSE and NOF calculated for the calibration period were 399 and 0.15, respectively. The RMSE and NOF calculated for the validation period were 600 and 0.44, respectively (Table 3).

[Insert Table 3 here]

3.2 Impact of hydrologic regime on DIN export

The variation in N exports from upstream to downstream in different land-use categories is shown in Fig. S2. N exports in the mainstream decreased under low streamflow conditions and increased under high flow conditions, indicating that DIN export was mainly controlled by hydrological regime. We used the moving-window method to evaluate the annual DIN export coefficients of various land-use patterns (Fig. 3). Farmland DIN export coefficients were higher under all runoff conditions. The DIN export coefficients of forests and orchards changed slightly and shared the same trend under the same conditions. The DIN export coefficients of built-up areas were high during wet years (i.e., with a runoff depth of more than 600 mm) and low during dry years (i.e., with a runoff depth of less than 400 mm).

[Insert Fig. 3 here]

The DIN export coefficients for forests, built-up areas, and orchards were positively elastic to runoff (Fig. 4). Though the DIN export coefficients of farmland were always high (Fig. 3), the annual runoff elasticity of farmland was low (Fig. 4), with a median value close to zero. The elasticity of built-up areas was the highest among the four land uses.

[Insert Fig. 4 here]

3.3 Pollution control scenario analysis

Based on the DIN export coefficients shown above, riverine DIN exports were estimated under different land-use policies with changing streamflow regimes. Increases in anthropogenic land use were predicted to increase riverine DIN export (Fig. 5). DIN exports in built-up areas were sensitive to changes in climatic conditions (i.e., dry and wet years; Fig. 5a).

[Insert Fig. 5 here]

4. Discussion

4.1 DIN export associated with mosaic land-use patterns

Relationships between land use and water quality have been proposed in a number of studies, with anthropogenic land use being negatively correlated to water quality and natural land use being positively correlated to water quality (Huang et al., 2012; Huang et al., 2016; Shih et al., 2016; Zhou et al., 2016; Liu et al., 2018). Our study confirmed these previously noted relationships and highlighted the capacity of export coefficient models to reliably evaluate N export in a catchment (Huang et al., 2012; Shih et al., 2016; Lian et al., 2018). The distinct linkage between DIN concentration and land use pattern in this catchment show necessity of determination of export coefficient for individual land (Fig. S1a). Agricultural activities, which are often associated with fertilizer application, are regarded as the major non-point source of riverine N exports, coupled with reductions in riparian and wetland areas (Huang et al., 2016; Li et al., 2019a). We observed the highest DIN export coefficients for agricultural land use (e.g., farmland: 9.16 mg/L), indicating that riverine DIN export from farmland (1,951 kg km-2 yr-1, derived from an annual discharge of 213 mm) accounted for about half of the riverine DIN export in the catchment. To put this number in context, the highest recorded riverine N exports from farmlands ranged from 400 to 3,265 kg km^{-2} yr^{-1} globally (Shields, 2008; Shih et al., 2016; Lian et al., 2018).

Although orchards are also a type of agricultural land use, their riverine DIN export coefficients were low compared to farmland and showed similar trends to those for forests (Fig. 3). Leaching and runoff are two major N export routes in catchments which may be controlled by the different land cover (Billy et al., 2013; de Girolamo et al., 2019). Indeed, although fertilizer was applied intensively to farmlands and orchards, trees grown in orchards tended to better retain N in the soil under the same hydrological regime(Fig. 3).

The lowest riverine DIN export was found for forests (619 kg km^{-2} yr^{-1}), though forests can remove or retain N efficiently (Fig. S1). The similar observations were conducted across China with annual deposition values of DIN as high as 1,318–1,521 kg km^{-2} yr^{-1} (Zhu et al., 2015; Zhang et al., 2018) and the natural processes in N cycle in wet subtropical environments(Shih et al., 2016).

4.2 Interactive impact from land use and hydrologic regime on riverine DIN export

It is difficult to evaluate the impacts of land use on riverine DIN export alone, since the coupled impacts of climate and associated hydrological variables should be considered, especially for long-term evaluations (Huang et al., 2013b; Zhou et al., 2017; Huang et al, 2018a; Ervinia et al., 2019). Hydrological regime is a holistic driver regulating material and energy flows in a catchment (Billy et al., 2013; de Girolamo et al., 2019), and storm events play an important role in N export. Increased discharge can drive N surplus in the soil, thus, an increase in N export is usually observed in wet years, especially during storm events (Kaushal et al., 2014; Huang et al., 2018).

The DIN export coefficient of built-up areas was linked to streamflow regime (Fig. 3), indicating it is necessary to evaluate coefficients under changing streamflow regimes. Compared with dry years, increased runoff in wet years can drive more DIN to the watershed (Fig. 5). Biogeochemical transformation may also decrease with increased runoff (Gallo et al, 2015; Greaver et al., 2016). Decreased N export can be observed mainstream in the Shixi catchment under the low flow condition. This trend was less visible under the high flow condition (Fig. S2). The major components of riverine DIN found in this study were ammonia nitrogen and nitrate nitrogen. The decreasing trend in ammonia nitrogen was more significant than that of nitrate nitrogen, since ammonia uptake is more preferential than nitrate. Thus, ammonia nitrogen’s fraction of DIN declines from the upstream to the downstream area. Nitrate nitrogen could accumulate in the catchment to promote greater microbial ammonia oxidation, as the ammonia oxidation rate is higher than the nitrite oxidation rate (Hong et al., 2018). Compared with the effect from biogeochemical transformation, land use was the major factor driving N export during storm events through changing headwater variability and hydrological connectivity (Kaushal et al., 2014).

It has been suggested that external ammonia nitrogen could be exported in a catchment when a river passes through an urban area as a result of sewage discharge (Simsek et al., 2012). The mainstream of the Shixi catchment also passes through an urban area, but elevated ammonia nitrogen was only observed in sites with high flow conditions (Fig. S2). In addition to sewage discharge, N from impervious surfaces in the urban area could be a source of N. Large amounts of N could be stored in impervious surfaces during the dry season or under low flow condition and be flushed out during the wet season or under high flow conditions (Kaushal et al., 2008; Kaushal et al., 2014; Huang et al., 2019). Our elasticity analysis revealed that DIN export coefficients from urban areas were high during wet years and low during dry years (Fig. 3).

Human-impacted areas tend to be more sensitive to inter-annual variability (including climate variability) than natural land-use types (Jiang et al., 2014; Ervinia et al., 2019). Riverine DIN exports for built-up areas and farmland were more sensitive to streamflow than those for forests. However, riverine DIN export found in orchards was less sensitive to streamflow change than that of forests (Fig. 4). The slope of catchment could be a critical factor inducing this phenomenon as poor water quality was observed in the high slope area (Li et al., 2019b).

4.3 Implications for watershed management

Our results can shed light on how to improve riverine N management in a catchment by considering the interactive effects of climate and land use. Our results can also be used to illustrate the evolution of biogeochemical cycles in response to changes in land use, management, and policy (Kaushal et al., 2014; Huang et al., 2018). Higher levels of riverine DIN exports were observed with increased runoff. Such amplification is proportional to anthropogenic N inputs associated with fertilizer applications and point-source pollution and should be emphasized for nitrogen reduction strategies during wet years. Built-up land was also a predominant factor in riverine DIN load (Shih et al., 2016). Built-up land can change the apportionment of inter-annual N export, which was negatively related to riverine DIN export during dry years and positively related to riverine DIN exports during wet years. In other words, changes in built-up area have the capacity to influence patterns of riverine DIN exports in this catchment.

5. Conclusion

This study proposed a framework to assess riverine DIN exports associated with changing land-use patterns and hydrological regimes. The proportion of human-impacted land use was negatively related to water quality. Though the DIN export coefficient of farmland was the highest among the four types of land use investigated, urbanization contributed to high runoff elasticity and high uncertainty. However, urbanized areas can rarely be converted to other uses, hence more attention may be paid to agricultural land management. The framework devised in this study can be used as an effective tool for water management.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This study was supported by the National Natural Science Foundation of China (Grant No. 41471154; Grant No. 41971231). Hefan Zeng, Juntao Cai, Boqiang Huang, Jihui Liu, and Cairong Xiao provided assistance with in-situ monitoring and experiments. We thank Dr Wang Shih-Chi from the US EPA for his assistance with writing the manuscript and anonymous reviewers for their constructive comments, which helped improve this paper.

References

Billy, C., Birgand, F., Ansart, P., Peschard, J., Sebilo, M., Tournebize, J., 2013. Factors controlling nitrate concentrations in surface waters of a artificially drained agricultural watershed. Landscape Ecology. 28: 665-684

Choi, H.T., Beven, K., 2007. Multi-period and multi-criteria model conditioning to reduce prediction uncertainty in an application of TOPMODEL within the GLUE framework. Journal of Hydrology. 332:316-336

de Girolamo, A.M., Spano, M., Ambrosio, E.D., Ricci, G.F., 2019. Developing a nitrogen load apportionment tool: theory and application. Agricultural Water Management. 226:105806

Delkash, M., Furat, A.M., AI-Faraj., Scholz, M., 2018. Impacts of anthropogenic land use changes on nutrient concentration in surface waterbodies: a review. Clean Soil Air Water. 46(5):1800051

Ervinia, A., Huang, J.L., Huang, Y.L., Lin, J.Y., 2019. Coupled effects of climate variability and land use pattern on surface water quality: An elasticity perspective and watershed health indicators. Science of the Total Environment. 693:133592

Ferguson, R.I., 1987. Accuracy and precision of methods for estimating river loads. Earth Surf. Process. Landforms 12: 95-104

Gallo, E.L., Meixner, T., Aoubid, H., Lohse, K.A., Brooks, P.D., 2015. Combined impact of catchment size, land cover, and precipitation on streamflow and total dissolved nitrogen: A global comparative analysis. Global Biogeochemical Cycles. 29(7):1109-1121

Galloway, J.N., Townsend, A.R., Erisman, J.W., Bekunda, M., Cai, Z., Freney, J.R., Martinelli, L.A., Steizinger, S.P., Sutton, M.A., 2008. Transformations of the nitrogen cycle: recent trends, questions, and potential solutions. Science. 2008 (320):889-892

Gall, W., Duftschmid, G., Dorda, W., 2001. Moving time window aggregates over patient histories. International Journal of Medical Informatics. 63:133-145

Gikas, G.D., 2014. Water quality of drainage canals and assessment of nutrient loads using QUAL2Kw. Environmental Processes. 1:369-385

Greaver, T.L., Clark, C.M., Compton, J.E., Vallano, D., Talhelm, A.F., Weaver, C.P., Band, L.E., Barson, J.S., Davidson, E.A., Tague, C.I., Felker-Quinn, E., Lynch, J.A., Herrick, J.D., Liu, I., Goodale, C.I., Novak, K.J., Haeuber, R.A., 2016. Key ecoligcal responses to nitrogen are altered by climate change. Nature Climate Change. 6:836-843

Huang, J.C., Lee, T.Y., Kao, S.J., Hsu, S.C., Lin, H.J., Peng, T.R., 2012. Land use effect and hydrological control on nitrate yield in subtropical mountainous watersheds. Hydrology & Earth System Science. 16:699-714

Huang, J.C., Lee, T.Y., Lin, T.C., Hein, T., Lee, L.C., Shih, T.Y., Kao, S.J., SHiah, F.K., Lin, N.H., 2016. Effects of different N sources on riverine DIN export and retention in a subtropical high-standing island, Taiwan. Biogeosciences. 6: 1787-1800

Huang, J.L., Zhou, P., Zhou, Z.R., Huang, Y.L., 2013a. Assessing the Influence of Land Use and Land Cover Datasets on Watershed Modeling in a Coastal Subtropical Watershed, Southeast China. International Journal of Environmental Research and Public Health. 10: 144-157

Huang, J.L., Zhang, Z.Y., Feng, Y., Hong, H.S., 2013b. Hydrologic response to climate change and human activities in subtropical coastal waershed of southeast China. Regional Environmental Change. 13(6): 1195–1210

Huang, J.L., Huang, Y.L., Pontius, R.G., Zhang, Z.Y., 2015. Geographically weighted regression to measure spatial variations in correlations between water pollution versus land use in a coastal watershed. Ocean & Coastal Management. 103:14-24

Huang, Y.L., Huang, J.L., Ervinia, A., Duan, S.W., Kaushal, S.K., 2018a. Land use and climate variability amplifies watershed nitrogen exports in coastal China. Ocean & Coastal Management. doi:

10.1016/j.ocecoaman.2018.02.024

Jackson-Blake, L.A., Sample, J.E., Wade, A.J., Helliwell, R.C., Skeffington, R.A., 2017. Are our dynamic water quality models too complex? A comparison of a new parsimonious phosphorus model, SimplyP, and INCA-P. Water Resource Research. 53:5382-5399

Jiang, J.P., Sharma, A., Sivakumar, B., Wang, P., 2014. A global assessment of climate-water quality relationships in large rivers: An elasticity perspective. Science of the Total Environment. 468-469:877-891

Kaushal, S.S., Groffman, P.M., Mayer, P.M., Striz, E., Gold, A,J., 2008 Effects of stream restoration on denification in an urbanizing watershed. Ecological Applications. 18: 789-804

Kaushal, S.S., Mayer, P.M., Vidon, P.G., Smith, R.M., Pennino, M.J., Newcomer, T.A., Duan, S.W., Welty, C., Belt, K.T., 2014. Land use and climate variability amplify carbon, nutrient, and contaminant pulses: a review with management implications. Journal of the American Water Resources Association. 50:585-614

Lee, M.J., Shevliakova, E., Malyshev, S., Milly, P.C., Jaffe, P.R., 2016. Climate variability and extremes, interacting with nitrogen storage, amplify eutrophication risk. Geophysical Research Letters. 43(11):7520-7528

Li, W.C., Liu, H.B., Zhai, L.M., Yen, H., Hu, W.L., Lei, Q.L., Stewart, R.J., Guo, S.F., Ren, T.Z., 2019a.Evaluation of concentration-discharge dynamics and nitrogen export on anthropogenic inputs and stormflow across alternative time-scales. Ecological Indicators. 98:879-887

Lian, H.S., Lei, Q.L., Zhang, X.Y., Yen, H., Wang, H.Y., Zhai, L.M., Liu, H.B., Huang, J.C., Ren, T.Z., Zhou, J.G., Qiu, W.W., 2018. Effects of anthropogenic activities on long-term changes of nitrogen budget in a plain river network region: a case study in the Taihu Basin. Science of the Total Environment. 645(15):1212-1220

Liu, J., She, Z.Y., Chen, L., 2018. Assessing how spatial variations of land use pattern affect water quality across a typical urbanized watershed in Beijing, China. Landscape and Urban Planning. 176:51-63

Mander, U., Kull, A., Kuusements, V., Toomas, T., 2000. Nutrient runoff dynamics in a rural catchment: influence of land use changes, climatic fluctuations and ecotechnological measures. Ecological Engineering. 14(4): 405-417

Mclauchlan, K.K., Williams, J.J., Craine, J.M., Jeffer, E,S., 2013. Changes in global nitrogen cycling during the Holocene epoch. Nature, 459(7441): 252-355

Packett, R., 2017. Rainfall contributes ~30% of the dissolved inorganic nitrogen exported from a southern Great Barrier Reef river basin. Marine Pollution Bulletin. 121(1-2):16-31

Parn, J., Henine, H., Kasak, K., Kauer, K., Sohar, K., Tournebize, J., Uuemaa, E., Valik, K., Mander, U., 2018. Nitrogen and phosphorus discharge from small agricultural catchments predicted from land use and hydroclimate. Land Use Policy. 75: 260-268

Preston, S.D., Bierman, V.J., Silliman, S.E., 1989. An evaluation of methods for the estimation of tributary mass loads. Water Resources Research. 25: 1379-1389

Sankarasubramanian, A., Richard, M.V., Limbrunner, J.F., 2001. Climate elasticity of streamflow in the United States. Water Resources Research. 37(6):1771-1781

Simsek, H., Kasi, M., Wahawan, T., Bye, C., Blonigen, M., Khan, E., 2012. Fate of dissolved organic nitrogen in two stage trickling filter process. Water Research. 46:5115-5126

State Environmental Protection Administrator of China (SEPAC)., 2002. Methods of monitoring and analyzing for water and wastewater, fourth ed. Chinese Environment Science Press

Shih, T.Y., Lee, T.Y., Huang, J.C., Kao, S.J., Chang, F.J., 2016 Apportioning riverine DIN load to export coefficients of land uses in an urbanized watershed. Science of the Total Environment. 560-561:1-11

Shields, C.A., 2008. Streamflow distribution of non-point source nitrogen export from urban-rural catchments in the CHesapeake Bay watershed. Water Resource Research. 44:W09416

Tomer, M.D., Meek, D.W., Jaynes, D.B., Hatfield, J.L., 2003. Evaluation of nitrate-nitrogen fluxes from a tile-drained watershed in central Iowa.Journal of Environmental Quality. 32:642-653

US EPA. 2001. User's manual of PLOAD version 3.0: An Arcview GIS tool to calcuate nonpoint sources of pollution in watershed and storm water projects.

Zhang, Q.Y., Wang, Q.F., Xu, L., Zhu, J.X,, He, N.P., 2018. Monthly dynamics of atmospheric wet nitrogen deposition on different spatial scales in China. Environmental Science & Pollution Research. 25:24417-24425

Zhang, Y.K., Schilling, K., 2005. Temporal variations and scaling of streamflow and baseflow and their nitrate-nitrogen concentration and loads. Advances in Water Resources. 28(7):701-710

Zhang, Z.Y., Huang, J.L., Zhou, M., Huang, Y.L., Lu, Y.M., 2019. A coupled modeling approach for water management in a river-reservoir system. International Journal of Environmental Research and Public Health. 16(16):2949

Zhang,Z.Y., Huang, J.L., Xiao, C.R., Huang, J.C. 2020. Simulation-based method to develop strategies for nitrogen pollution control in a creek watershed with sparse data. Environment Science and Pollution Research, DOI: 10.1007/s11356-020-09954-z

Zhou, Y., Xu, J.F., Yin, W., Ai, L., Fang, N.F., Tan, W.F., Yan, F.L., Shi, Z.H., 2017. Hydrological and environmental controls of the stream nitrate concentration and flux in a small agricultural watershed. Journal of Hydrology. 545:355-366

Zhou, P., Huang, J.L., Pontius, R.G., Hong, H.S., 2016. New Insight into the Correlations between Land Use and Water Quality in a Coastal Watershed of China: Does Point Source Pollution Weaken It? Science of the Total Environment. 543: 591-600

Zhou, P., Huang, J.L., Hong, H.S., 2018. Modeling nutrient sources, transport and management strategies in a coastal watershed, Southeast China. Science of the Total Environment. 610-611:1298-

1309

Zhu, J.X., He, N.P., Wang, Q.F., Yuan, G.F., Wen, D., Yu, G.R., Jia, Y.L., 2015. The composition, spatial patterns, and influencing factors of atmospheric wet nitrogen deposition in Chinese terrestrial ecosystems. Science of the Total Environment. 511:777-785