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Key Points:
- A dynamic watershed model is developed to address the transient N storage effect
- Legacy anthropogenic N can contribute a dominative N flux to rivers
- Long-term fate and transport of anthropogenic N inputs are determined

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A dynamic watershed model for determining the effects of transient storage on nitrogen export to rivers

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Abstract Legacy anthropogenic nitrogen (N) has been suggested as a major cause for increasing riverine N exports despite significant declines in anthropogenic N inputs in many regions. However, little quantitative knowledge exists concerning the contribution of the legacy N pool to riverine N export. This study developed a dynamic watershed N delivery model to address the role of transient storage of anthropogenic N inputs on riverine N flux. Employing simple mass balance and equivalent substitution rules, the model expresses the transient storage of legacy N mass with a term that combines the previous one year's riverine total N (TN) flux, relevant explanatory variables, and unknown parameters, enabling us to inversely calibrate the model parameters from measurable variables using Bayesian statistics. The model efficacy was demonstrated through application to the Yong'an River watershed in eastern China based on a 31 year record (1980–2010) of riverine TN fluxes. The model can quantify annual transient storage of legacy N and its resulting contribution to annual riverine N flux. The model also allows partitioning of the complete long-term mass balance for the fate (e.g., transient storage, riverine export, and loss/retention by denitrification, biomass uptake and wood product export) of annual anthropogenic N inputs. To further improve the model, various N input-output processes can be specified and long-term measurements of N fates are required to further verify the model results. This study demonstrates the need to consider transient storage effects as an improvement to current watershed models and for developing and assessing N pollution control measures.

1. Introduction

Excessive riverine nitrogen (N) is an increasing concern worldwide, as it degrades aquatic ecosystem health, decreases water quality for several beneficial uses, and causes eutrophication and hypoxia in coastal waters [*Alam and Goodall*, 2012; *Howarth et al.*, 2012; *Bouraoui and Grizzetti*, 2014]. Increasing anthropogenic N application to lands to an extent that exceeds the ecosystem's ability to retain N has been recognized as a major cause of increasing N levels observed in rivers [*Galloway et al.*, 2004; *Williams et al.*, 2004; *Howarth*, 2008; *Schlesinger*, 2009]. Riverine N levels continue to increase in many areas in recent decades even after a significant decline in anthropogenic N inputs with the implementation of the Clean Water Act (1972) in the United States and the Nitrate Directive (1991) in Europe [*Albiac*, 2009; *Worrall et al.*, 2009; *Dubrovsky and Hamilton*, 2010; *Argerich et al.*, 2013; *Bouraoui and Grizzetti*, 2014]. A primary reason for these limited results is the contribution of legacy N that is transiently stored in the soil, vadose zone, and groundwater [*McIsaac et al.*, 2001; *Williams et al.*, 2004; *Gardner and Drinkwater*, 2009; *Howden et al.*, 2011; *Sanford and Pope*, 2013; *Kopáček et al.*, 2013], due to the long transit times (ranging from years to decades) for N passing through watersheds to rivers [*Meals et al.*, 2010; *Sebilo et al.*, 2013; *Tesoriero et al.*, 2013; *Bouraoui and Grizzetti*, 2014]. The transient storage of N in watersheds has been recognized as a missing source contributing to riverine N flux, as well as a missing sink for anthropogenic N inputs in watershed N budgets [*Bartoli et al.*, 2012; *Vogt et al.*, 2013; *Yanai et al.*, 2013; *Chen et al.*, 2014].

The transient storage of legacy N in this study refers to the surplus anthropogenic N inputs from previous years that is temporarily stored in watershed landscapes (e.g., soil, vadose zone, groundwater and river sediment), is actively cycled, and has the potential to contribute N to atmosphere, biomass, and river fluxes in future years. The magnitude of transient N storage within a given watershed is time dependent and is

regulated by processes affecting the fate and transport of N within the watershed. Therefore, understanding the effects of transient storage on the N input-output balance is critical for determining the time period over which N is temporarily stored and re-released in response to human activities and climate change [*Van Breemen et al*., 2002; *Howarth*, 2008; *Swaney et al*., 2012]. In terms of water quality management, quantitative information concerning the transient storage effect is required for developing and evaluating watershed N pollution control measures and schedules to optimize pollution control expenditures for maximum return on investment [*Sanford and Pope*, 2013; *Bouraoui and Grizzetti*, 2014]. However, there is a paucity of quantitative knowledge concerning such transient storage effects on riverine N flux at the watershed scale. Due to the difficulty in measuring watershed denitrification and N accumulation rates across spatially and temporally heterogeneous landscapes (e.g., vegetation, soils, and aquifers) [*Howarth*, 2008], it is nearly impossible to measure the transient storage of legacy N and its contribution to riverine N flux using standard monitoring approaches. Thus, the ability to model these effects provides a powerful tool for assessing the fate and transport of legacy N over time and space.

Numerical models, ranging from lumped watershed models, such as the export coefficient model, SPARROW, GlobalNEWS, and PolFlow, and mechanistic models, such as AGNPS, HSPF, and SWAT [*Smith et al*., 1997; *de Wit et al*., 2000; *Borah and Bera*, 2004; *Wellen et al*., 2012; *Bouraoui and Grizzetti*, 2014; *Wang et al*., 2014], are available for quantifying the impact of anthropogenic N inputs on riverine N fluxes at the watershed scale. However, there is considerable uncertainty in calibrating these watershed models using commonly available watershed monitoring data, since the measured riverine N concentration is a mixture of N having different ages, and very often the residence time of N in landscapes is much larger than the temporal extent of the calibration data available [*Meals et al*., 2010; *Howden et al*., 2011]. Mechanistic models typically require a large amount of data for calibration of many parameters (much of this data requiring specialized studies to obtain), making their implementation difficult for many watersheds [*Borah and Bera*, 2004; *Wellen et al*., 2012; *Chen et al*., 2013]. The effects of transient storage on N cycling and transport are not well addressed and formulated in most current watershed mechanistic models [*Meals et al*., 2010; *Sanford and Pope*, 2013; *Bouraoui and Grizzetti*, 2014] due to the limited quantitative knowledge concerning residence time and biogeochemical mechanisms for N passing through watersheds to the river network [*Hamilton*, 2012; *Sebilo et al*., 2013]. Lumped watershed models and the net anthropogenic N inputs (NANI) budgeting approach generally assume that the N status of soils, aquifers, and biomass is at steady state (at least over a multiyear period) [*Howarth et al*., 2006; *Alam and Goodall*, 2012; *Swaney et al*., 2012; *Wellen et al*., 2012]. Thus, they are commonly applied using a multiyear average temporal resolution to avoid the uncertainty derived from the N leaching lag effect. However, a major challenge remains in determining the appropriate length of the multiyear period that should be used to estimate N source inputs to satisfy the steady state assumption [*Chen et al*., 2014]. Overall, current watershed models do not effectively represent the effects of transient storage for anthropogenic N inputs on riverine export. Thus, a simple and effective model would provide a powerful tool for assessing N reduction strategies at the watershed scale.

This study developed a novel, dynamic watershed N delivery model for quantifying transient storage of legacy N and its resulting riverine TN flux as well as determining anthropogenic N fates (e.g., riverine export, storage in watersheds, and loss/retention via denitrification, biomass uptake and wood product export) over time. Employing simple mass balance and equivalent substitution rules, this model expresses annual transient storage of legacy N with a term combining the previous year's riverine TN flux and three unknown parameters, enabling us to inversely calibrate the model parameters from measurable variables using Bayesian statistics. The efficacy of this model was demonstrated through application to a 31 year water quality record (1980–2010) from the Yong'an River watershed in eastern China. The findings of this study provide researchers and managers with critical knowledge to improve watershed N modeling and to develop and assess efficient N pollution control measures.

2. Materials and Methods

2.1. Watershed Description

The Yong'an River watershed is located in the highly developed Taizhou City of Zhejiang Province, China (Figure 1). The Yong'an River flows into Taizhou Estuary and the East China Sea, a coastal area that commonly experiences hypoxia. The sampling location for this study was 55 km upstream of Taizhou Estuary.

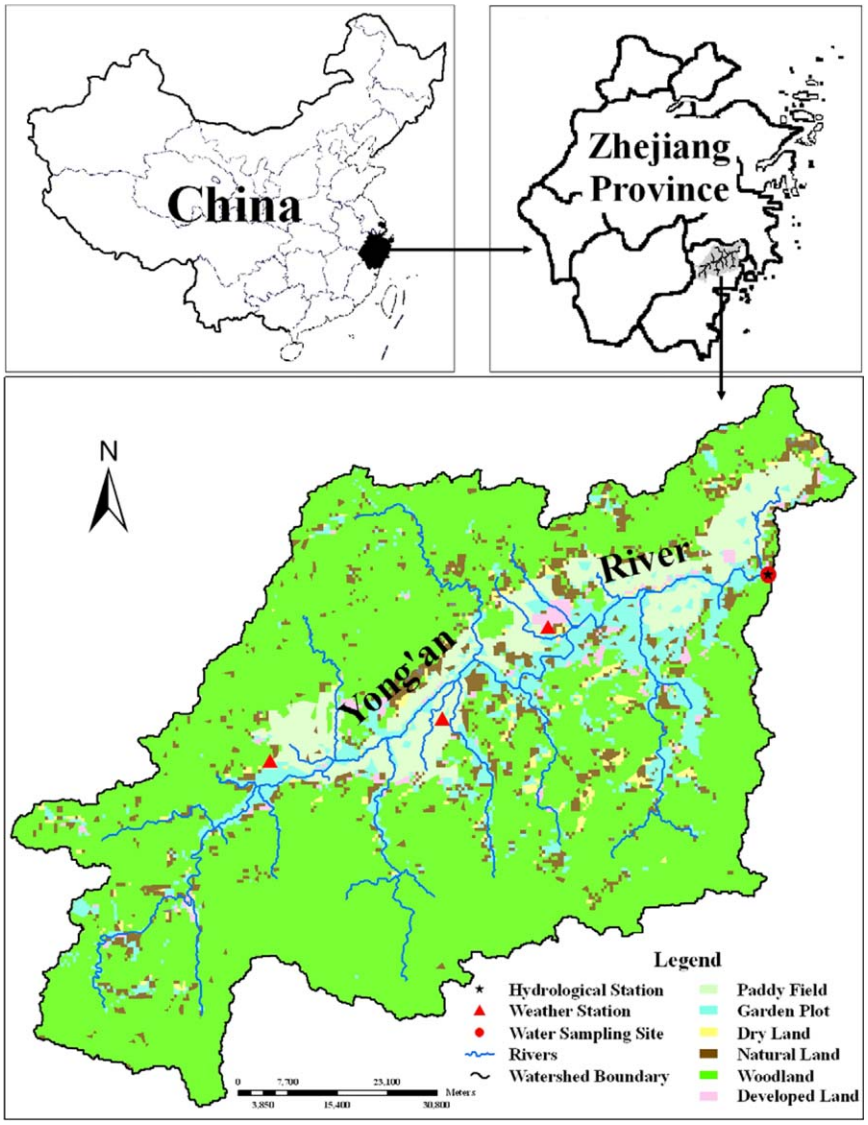

Figure 1. Location of Yong'an River watershed in China and Zhejiang Province, water quality sampling site and weather stations, and land-use distribution in 2009.

The river drains a total area of 2474 km^2 and has an average annual water depth of 5.42 m and discharge of 72.9 m^3 s^{-1} at the sampling location. There is no river regulation in the studied watershed, such as dams/reservoirs and transboundary water withdrawal facilities. The climate is subtropical monsoon having an average annual temperature of 17.4°C and average annual precipitation of 1400 mm (Figure 2a). Rainfall mainly occurs in May–September with a typhoon season in July–September. Agricultural land (e.g., paddy field, garden plot, and dry land) averaged ~12% of total watershed area, with developed land (e.g., rural and urban residential, roads, mining and industrial), woodland, and barren land contributing ~3%, ~67%, and ~18%, respectively (Figure 1). The economic role of agriculture has been increasingly replaced by industry since the 1990s, resulting in a remarkable reduction (~40%) in chemical N fertilizer application due to decreased crop cultivation area (~44%) since 2000 (Figure 2b). Due to recent replacement of the old agricultural irrigation and drainage system (constructed with stone and mud in the 1950s), the agricultural land area irrigated and drained with cement channels and pipes increased ~2-fold since 2000 (Figure 2c).

2.2. Data Sources

River water samples were collected once every 4−8 weeks (n=250 sampling times total) at Baizhiao station from 1980 to 2010 (Figure 1) by the Taizhou City Environment Protection Bureau. A well-mixed, composite

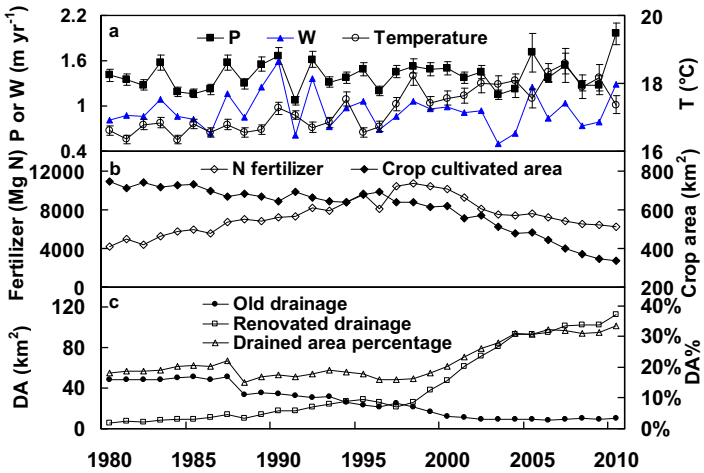

Figure 2. Historical trends for (a) annual precipitation (*P*), water yield (*W*), temperature (T), (b) N fertilizer application and cultivated crop area, and (c) drained agricultural land area (DA) and percentage (DA%) in Yong'an River watershed in 1980−2010. Error bars refer to standard deviation of measurements from three weather monitoring sites within the watershed.

water sample (surface and bottom layers at three sites along the cross section) was collected between 8:00 and 9:00 on each sampling date, and total nitrogen (TN) and nitrate concentrations were analyzed by the Taizhou City Environment Protection Bureau. Duplicate samples from the composite sample were acidified with H_2SO_4 in the field (10 ml of concentrated H_2SO_4 per liter) and filtered and analyzed within 4 hr of sampling. Nitrate and TN were determined using the spectrophotometric phenol disulfonic acid method and persulfate digestion using the UV spectrophotometric method, respectively [*Chen et al.*, 2014].

Daily river discharge and annual precipitation were obtained from the local Hydrology Bureau and Weather Bureau, respectively. Daily river water discharge records in 1980−2010 were divided into high (0−30%), medium (30−70%), and low flow (70−100%) regimes using the duration curve method [*Chen et al.*, 2012].

Extensive soil samples (one composite sample per 15 ha for plain regions and one composite sample per 25 ha for hilly regions) were collected from the top 20 cm layer of agricultural lands in the watershed by the local Agriculture Bureau in 1984 and 2009 [*Soil Survey Office of Taizhou City*, 1987; *Chen and Lu*, 2013; *Agricultural Bureau of Xianju County*, 2011]. Bulk density (n=195) and available N (KCl-extractable $NH_4 + NO_3$; n=236) for the time-paired soil samples were used to determine the change in available N mass (i.e., a measure of transiently stored N in soil) between 1984 and 2009.

Data sources for estimating the annual net anthropogenic nitrogen input (NANI) budget for the Yong'an River watershed from 1980 to 2010 were derived from the annual Statistic Yearbook for Xianju County and Linhai City. By defining the watershed boundary using a geographic information system (GIS), total annual anthropogenic N sources and sinks for the Yong'an River watershed were summarized for Xianju County (∼73% of total watershed area) and three towns within Linhai City (∼12% of total watershed area). In the remaining ∼15% of the catchment area, we only considered the N input from atmospheric deposition in the NANI analysis, since it was dominated by forests (∼95%) and fell within Panan County (located in the northwest portion of the watershed) and Jinyun County (located in the southwest portion of the watershed) (Figure 1).

2.3. Riverine TN Flux Estimate

To estimate annual TN flux using the discrete TN concentration monitoring data from 1980 to 2010, the widely applied LOADEST model was utilized to predict daily TN concentration [*Runkel et al.*, 2004]. In this study, seven LOADEST model parameters were calibrated by least squares fitting using Matlab software (version 10.0, The MathWorks, Inc., USA, 2010). All calibrated parameter values were statistically significant ($p<0.001$) with an average relative errors of ±5% and high R^2 between the modeled and measured TN concentration ($R^2=0.73$, $p<0.001$, n=250). These results indicated that the established LOADEST model can be reasonably applied to predict daily TN concentration in the Yong'an River. Based on the predicted daily TN concentration, daily TN load was estimated by multiplying TN concentration and water discharge, and the annual TN load was calculated as the sum of daily TN loads for a corresponding year. Annual TN flux was then determined by dividing annual TN load by the total watershed area.

2.4. Net Anthropogenic Nitrogen Inputs (NANI) Estimate and Uncertainty Analysis

The NANI budget estimates the human-controlled N inputs to a watershed and was calculated as the sum of five major components: atmospheric N deposition, fertilizer N application, agricultural N fixation, seed N

input, and net N in food and feed import/export [*Howarth*, 2008; *Han et al*., 2011, 2014]. Wastewater discharges are not considered explicitly in the NANI analysis, since the N in wastewater originates from food and feed (either imported or grown within the region, with the source nitrogen from fertilizer or agricultural nitrogen fixation) [*Howarth et al*., 2006]. Net N food and feed balance was composed of crop and livestock production, and N consumption by livestock and humans. The majority of parameters required for NANI estimation were derived from relevant published literature for China (Table 1). The per capita intake of protein by humans for each year was derived from *Han et al*. [2014], i.e., 3.92, 4.67, 4.75 and 4.58 kg N in 1981, 1990, 2000, and 2009, respectively. We linearly interpolated values for missing years using the reported values. The life cycle for each animal type was adopted from *Wang et al*. [2006]. All animals were completely formula fed, i.e., 50% from corn and 50% from pasture [*Li et al*., 2007]. We assume that pests, spoilage, and processing caused a 10% loss for all crops and spoilage and inedible components caused a 10% loss of animal products available for consumption [*Han et al*., 2011, 2014]. Atmospheric N deposition was obtained from annual average N deposition rates reported for southeast China in 1980–2010 by *Liu et al*. [2013] and for Zhejiang Province in 1981–2009 by *Han et al*. [2014]. The only atmospheric input considered was NO_y deposition (sum of NO, NO_2, HNO_3, and NO_3^-), which usually originates largely from fossil-fuel combustion and is therefore a new input of N to the watershed [*Howarth*, 2008; *Han et al*., 2014]. This assumptions is well supported by studies in nearby regions of China, where NO_y emission fluxes accounted for $<$1.5% of the fertilizer N applied [*Zhao et al*., 2009; *Yan et al*., 2011; *Ti et al*., 2012]. Deposition of N does not include ammonia, given that most of the ammonia in the atmosphere is deposited near the site of emission to the atmosphere and originates from agricultural sources already included in the NANI budget [*Howarth et al*., 2006; *Han et al*., 2011, 2014].

To gain insight into the uncertainty in the NANI estimation, an uncertainty analysis was performed using Monte Carlo simulation, which utilized a random sampling from probability distribution functions as input [*Yan et al*., 2011]. Due to the limited information available for China and surrounding regions, we can not rigorously determine the probability distribution and coefficient of variation for each parameter used in estimating NANI. Therefore, we assumed that all the parameters used in the NANI estimation followed a normal distribution with a coefficient of variation equal to 30% for each parameter, which is commonly used in N budgeting studies of nearby watersheds [*Yan et al*., 2011; *Ti et al*., 2012]. All input parameters (Table 1) for estimating NANI were set to be independent of each other during the Monte Carlo sampling, since the majority of the parameters have no cause-and-effect relationship with each other in theory and the dependence (correlation) is difficult to quantify due to the limited information. The Monte Carlo sampling

Table 1. Coefficient Values for Estimating Annual Net Anthropogenic Nitrogen Inputs in the Yong'an River Watershed

N Fixation Rate (kg N ha^{-1} yr^{-1})[a]		Seed N Input Rate (kg N ha^{-1} yr^{-1})[b]	
Land Types	N Fixation	Crop Type	Seed N Input
Green manure	150	Rice	0.69
Leguminous plants	64	Wheat	2.27
Paddy field	45	Corn	0.26
Dryland	15	Potato	1.07
Garden plot	15	Soybeans	1.08
		Peanuts	0.35
		Vegetables	0.03

Animal N Consumption and Excretion (kg N $Individual^{-1}$ yr^{-1})[c]				N content of Crop Production (g kg^{-1})[d]	
Animal Type	N Consumption	N Excretion	Production N	Crop Type	N Content
Pigs and hogs	16.7	11.5	5.17	Rice	11.8
Cattle	54.8	48.8	6.03	Corn	14.1
Sheep	6.85	5.75	1.10	Wheat	17.9
Chickens	0.57	0.37	0.20	Potato	3.2
Duck	0.63	0.41	0.22	Peanuts	19.4
Aquatic products	34.4	4.96	29.4	Soybeans	56.2
				Vegetable	2.6
				Fruits	0.59

[a]*Yan et al*. [2011] and *Ti et al*. [2012].
[b]*Han et al*. [2011, 2014].
[c]*Wang et al*. [2006] and *Li* [2007].
[d]*Han et al*. [2011, 2014].

method was used to randomly generate 10,000 sets of model parameters according to their normal distribution functions, resulting in 10,000 iterations of NANI simulation for each year to obtain the mean and 95% confidence interval for annual NANI values. The NANI estimation procedure was formulated in Microsoft Excel 2007 embedded with Crystal Ball software (Professional Edition 2000, Oracle Ltd. USA, 2000) to run Monte Carlo simulations.

2.5. Development of the Dynamic Watershed Nitrogen Delivery Model

2.5.1. Derivation of the Model

This study assumes that new NANI (kg N ha^{-1} yr^{-1}) and legacy N in transient storage (S_t, kg N ha^{-1} yr^{-1}) from each year would experience the same fate (e.g., riverine export; storage in soil, groundwater and river sediment; and denitrification, nonharvested biomass uptake and wood product removal) [*Van Breemen et al.*, 2002; *Cui et al.*, 2013; *Yanai et al.*, 2013] during a certain time interval ($\triangle t$, i.e., 1 year here). Accordingly, we developed the following dynamic model that incorporates the contribution of annual new NANI, S_t, and natural background sources (B_t, kg N ha^{-1} yr^{-1}) for riverine TN flux (F_t, kg N ha^{-1} yr^{-1}):

$$F_t = \alpha_t (NANI_t + S_t) + B_t \tag{1}$$

where subscript t denotes the tth year; α_t (dimensionless, $0<\alpha_t<1$) represents the annual riverine export fraction of $NANI_t$ and S_t. Analogically, riverine TN flux in the previous one year (F_{t-1}, kg N ha^{-1} yr^{-1}) can be estimated as:

$$F_{t\text{-}1} = \alpha_{t\text{-}1} (NANI_{t\text{-}1} + S_{t\text{-}1}) + B_{t-1} \tag{2}$$

where the subscript $t-1$ denotes the previous year's value.

Based on the mass balance, the change of S within a given year is determined by NANI and outputs via riverine export, denitrification, nonharvested biomass uptake and wood product export. Here N loss via riverine export and other pathways is individually integrated as a first-order reaction. Accordingly, the relationship between S_t and S_{t-1} follows:

$$S_t = (NANI_{t-1} + S_{t-1}) \exp(-\beta_{t-1}\Delta t - \theta_{t-1}\Delta t) \tag{3}$$

where β and θ denotes the first-order rate coefficients for export by river and loss by denitrification, nonharvested biomass uptake and wood product export, respectively. Accordingly, the riverine export fraction α_t in equation (1) can be further expressed as:

$$\alpha_t = 1 - \exp(-\beta_t \Delta t) \tag{4}$$

In practice, S_t or S_{t-1} is very difficult to unambiguously measure by common monitoring and calculation approaches. Based on the equivalent substitution rule, S_t in equation (1) can be expressed by measurable variables and parameters through combining equations (2) and (3), which yields:

$$F_t = [1 - \exp(-\beta_t \Delta t)]\{NANI_t + (F_{t-1} - B_{t-1}) \exp(-\beta_{t-1}\Delta t - \theta_{t-1}\Delta t)/[1 - \exp(-\beta_{t-1}\Delta t)]\} + B_t \tag{5}$$

Equation (5) contains several measurable variables ($NANI_t$, F_t, and F_{t-1}), and the parameters β, θ, and B can be calibrated in practice. In this study, equation (5) was defined as a dynamic watershed N delivery model, which expresses the contributions of transient N storage, NANI and background N sources to annual riverine N flux.

2.5.2. Model Parameterization

To express parameters β and θ in equation (5) by measurable temporal watershed attributes, a parameterization methodology from previous lumped watershed models was adopted [*Smith et al.*, 1997; *Grizzetti et al.*, 2005; *Wellen et al.*, 2012; *Chen et al.*, 2013]:

$$\beta_t = \sum_{i=1}^{n} a_i \gamma_{i,t}; \quad \theta_t = \sum_{j=1}^{m} b_j \lambda_{j,t} \tag{6}$$

where $\gamma_{i,t}$ and $\lambda_{j,t}$ denote the ith and jth temporal watershed attributes that influence the river export rate and loss rate from denitrification, biomass uptake and wood product export, respectively. a_i (years) and b_j (years) denote the unknown coefficients for the corresponding watershed attributes.

Riverine TN flux derived from natural background sources (B_t, kg N ha^{-1} yr^{-1}) is assumed as a function of annual average river discharge (Q_t, m^3 s^{-1}) and natural background river N concentration (C_b, mg N L^{-1}), which

is supported by studies showing that the observed riverine N flux strongly depends on annual discharge in a number of minimally disturbed watersheds [*Lewis et al*., 1999; *Howarth et al*., 2006; *Han et al*., 2009]:

$$B_t = 86.4\, NQ_t C_b / A \tag{7}$$

where N is the number of days in a year (i.e., 365 or 366), A is the watershed area (ha), and 86.4 is a conversion factor.

2.5.3. Model Calibration

A Bayesian statistical approach coupled with the Markov Chain Monte Carlo (MCMC) algorithm was adopted to inversely calibrate the unknown model coefficients a_i, b_j, and C_b in model equation (5) from measurable variables using WinBUGS 1.4 [*Chen et al*., 2012; *Wellen et al*., 2012]. A detailed description of the Bayesian calibration procedures for relevant water quality model parameters (e.g., formulating the prior probability distributions for targeted parameters, specifying the likelihood function, and MCMC sampling for the posterior probability distributions) as well as the code for WinBUGS software is available in *Chen et al*. [2012] and *Wellen et al*. [2012]. Based on previous studies, the prior distribution for each of the three unknown coefficients was assumed to follow a normal distribution [*Chen et al*., 2013], i.e., a_i: 0.2 $\pm$ 0.2 years [*Howarth et al*., 2006, 2012; *Swaney et al*., 2012; *Chen et al*., 2014]; b_j: 0.6 $\pm$ 0.6 years [*Van Breemen et al*., 2002; *Yan et al*., 2011; *Ti et al*., 2012; *Wang et al*., 2014]; C_b: 0.15 $\pm$ 0.1 mg N L^{-1} [*Meybeck*, 1982]. To obtain the best-fit posterior model coefficients for a_i, b_j, and C_b, two Markov chains were initiated at different arbitrary initial values for each coefficient. The generated posterior distributions for the three coefficients were all based on 10,000 MCMC samples until the model successfully converged (i.e., Monte Carlo errors $<$10% of standard deviations). The first 5000 runs were discarded after model convergence and then a total of 1000 samples for each unknown quantity were randomly taken from the next 5000 iterations to reduce autocorrelation [*Chen et al*., 2013]. The agreement between annual TN fluxes estimated by LOADEST and modeled by equation (5) was evaluated using correlation (R^2) and Nash–Sutcliffe coefficients [*Borah and Bera*, 2004; *Moriasi et al*., 2007].

In this model calibration, three major temporal watershed attributes, namely annual water yield [*McIsaac et al*., 2001; *de Wit et al*., 2000; *Howarth et al*., 2006, 2012; *Han et al*., 2009; *Alam and Goodall*, 2012], urban land area percentage [*Han et al*., 2009], and drained agricultural land area percentage [*Kopáček et al*., 2013; *Chen et al*., 2014], were considered as potential influencing factors for the first-order loss rate coefficient for riverine export (β). Also, three major temporal watershed attributes, such as annual average temperature [*Smith et al*., 1997; *Schaefer and Alber*, 2007; *Alam and Goodall*, 2012], drained agricultural land area percentage [*Kopáček et al*., 2013], and annual water yield [*Grizzetti et al*., 2005; *Howden et al*., 2011; *Howarth et al*., 2012; *Wellen et al*., 2012], were considered as potential influencing factors for the first-order loss rate coefficient for denitrification, nonharvested biomass uptake and wood product export (θ). Due to the close relationship between annual water yield and precipitation (R^2=0.95**, $p<0.01$) in the Yong'an River watershed, only annual water yield was considered in this study. To determine the most efficient explanatory variables for the model, the potential explanatory variables mentioned above were added one by one for the β and θ parameters shown in equation (5) for calibrating unknown coefficients a_i, b_j, and C_b using Bayesian statistics. The best set of explanatory variables was determined according to model agreement. All individual attributes used for calibration were reduced to the same scale by scaling as a function of the maximum value for the study period [*Grizzetti et al*., 2005; *Chen et al*., 2013].

2.5.4. Posterior Simulations of Annual NANI Fate

Based on equations (1), equation (3), and the calibrated posterior parameters β and θ or a_i and b_j from equation (5), the annual NANI export by rivers (FN_t, kg N ha^{-1} yr^{-1}), transient storage (SN_t, kg N ha^{-1} yr^{-1}), and loss/storage via denitrification, nonharvested biomass uptake and wood product export (LN_t, kg N ha^{-1} yr^{-1}) in the current year can be estimated as follows:

$$FN_t = [1 - \exp(-\beta_t \Delta t)] NANI_t \tag{8}$$

$$SN_t = NANI_t \exp(-\beta_t \Delta t - \theta_t \Delta t) \tag{9}$$

$$LN_t = [\exp(-\beta_t \Delta t) - \exp(-\beta_t \Delta t - \theta_t \Delta t)] NANI_t \tag{10}$$

Then, annual NANI export by rivers (FN_{t+i}, kg N ha^{-1} yr^{-1}), transient storage (SN_{t+i}, kg N ha^{-1} yr^{-1}), and loss/storage via denitrification, nonharvested biomass uptake and wood product export (LN_{t+i}, kg N ha^{-1} yr^{-1}) in the succeeding ith year can be estimated as follows:

$$FN_{t+i}=[1-\exp(-\beta_{t+i}\Delta t)]NANI_t\exp[-\sum_{i=1}^{n}(\beta_{t+i-1}+\theta_{t+i-1})\Delta t] \tag{11}$$

$$SN_{t+1}=NANI_t\exp[-\sum_{i=1}^{n}(\beta_{t+i}+\theta_{t+i})\Delta t] \tag{12}$$

$$LN_{t+i}=\{\exp(-\sum_{i=1}^{n}\beta_{t+i}\Delta t)-\exp[-\sum_{i=1}^{n}(\beta_{t+i}+\theta_{t+i})\Delta t]\}NANI_t\exp[-\sum_{i=1}^{n}(\beta_{t+i-1}+\theta_{t+t-1})\Delta t] \tag{13}$$

2.5.5. Posterior Simulations of Annual Watershed Transient Storage N Mass

Based on the calibrated posterior parameters β and θ or a_i and b_j from equation (5), the initial watershed transient storage of N (S_t) in 1980 was estimated inversely from equation (1):

$$S_t=(F_t-B_t)/[1-\exp(-\beta_t\Delta t)]-NANI_t \tag{14}$$

Based on S_t, the watershed transient N storage in each of the succeeding years was estimated for the 1981−2010 period using equation (3).

3. Results

3.1. Dynamic Watershed N Delivery Model Calibration

When annual water yield was considered as the influencing factor for β and annual average temperature as the influencing factor for θ in calibrating equation (5) using Bayesian statistics, the calibrated coefficients a_i, b_j, and C_b were highly statistically significant ($p<0.001$) and had small Monte Carlo errors (<1% of standard deviations) (Table 2). The resulting posterior parameters yielded a high agreement between riverine TN fluxes modeled by equation (5) and those estimated by LOADEST with a high R^2 value (0.91) and Nash-Sutcliffe coefficient (0.90) (Figure 3a). Relative errors for mean modeled annual TN fluxes were less than 7% and the interquartile range for each year was relatively symmetrical, typically ranging from −20% to +20%. Plots of predicted values and residuals determined by the model indicated that the residual interval was not correlated with the variance of the mean flux (Figure 3b, $p=0.25$). Further consideration of annual drained agricultural land area percentage and developed land area percentage as explanatory variables for β and θ did not improve the model's predictive capability, as indicated by their R^2 values (<0.80) and Nash-Sutcliffe coefficients (<0.75). Therefore, this study only considered water yield and temperature as the influencing watershed attributes in model equation (5).

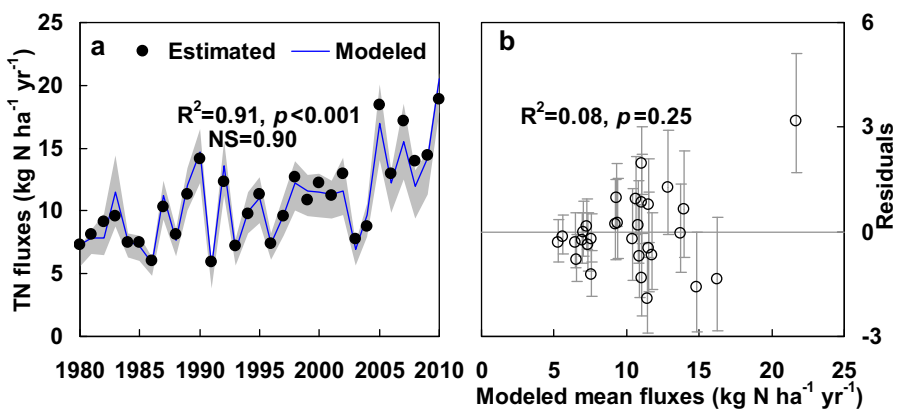

Figure 3. LOADEST estimated versus modeled riverine TN flux using the (a) calibrated dynamic watershed N delivery model and (b) residual values plotted against the modeled mean riverine TN flux for the Yong'an River watershed in 1980–2010. Shadow area and error bar denote the 95% confidence interval of the fluxes and residuals, respectively. NS denotes Nash-Sutcliffe coefficient.

Table 2. Calibrated Parameters for the Dynamic Watershed N Model Using the Bayesian Statistical Approach for the Yong'an River Watershed

Parameters	Unit	2.5%	Mean	Median	97.5%	Standard Deviation	Monte Carlo Error
a_i	years	0.021	0.029	0.031	0.046	0.0092	1.77E-04
b_j	years	0.070	0.107	0.120	0.147	0.0304	6.20E-04
C_b	mg N L^{-1}	0.078	0.146	0.152	0.239	0.0574	6.29E-04

3.2. Anthropogenic Nitrogen Input Source and Sink Dynamics

In the Yong'an River watershed, estimated mean NANI increased from 38.0 kg N ha^{-1} yr^{-1} (95% uncertainty range: 34.4−41.7 kg N ha^{-1} yr^{-1}) in 1980 to 77.6 kg N ha^{-1} yr^{-1} (95% uncertainty range: 72.9−82.3 kg N ha^{-1} yr^{-1}) in 2000 before declining to 67.3 kg N ha^{-1} yr^{-1} (95% uncertainty range: 62.2−72.4 kg N ha^{-1} yr^{-1}) in 2010 (Figure 4a). In the 2000s, NANI showed a decreasing trend due to decreased chemical N fertilizer application and agricultural biological N fixation resulting from decreased total crop cultivation area (∼44%, Figure 2). The magnitude and relative importance of individual N inputs varied over the study period with fertilizer (47.9%) and atmospheric N deposition (39.3%) being the major N sources (Figure 4a). The contribution from agricultural N fixation (7.8%) and seed input (0.4%) steadily decreased, while net food and feed N input increased remarkably and accounted for 4.6% of NANI.

Usingequation (8) and calibrated model parameters, estimated mean riverine export of annual NANI from the current year was 1.1 kg N ha^{-1} yr^{-1} (mean range: 0.5−1.6 kg N ha^{-1} yr^{-1}) (Figure 4b), which

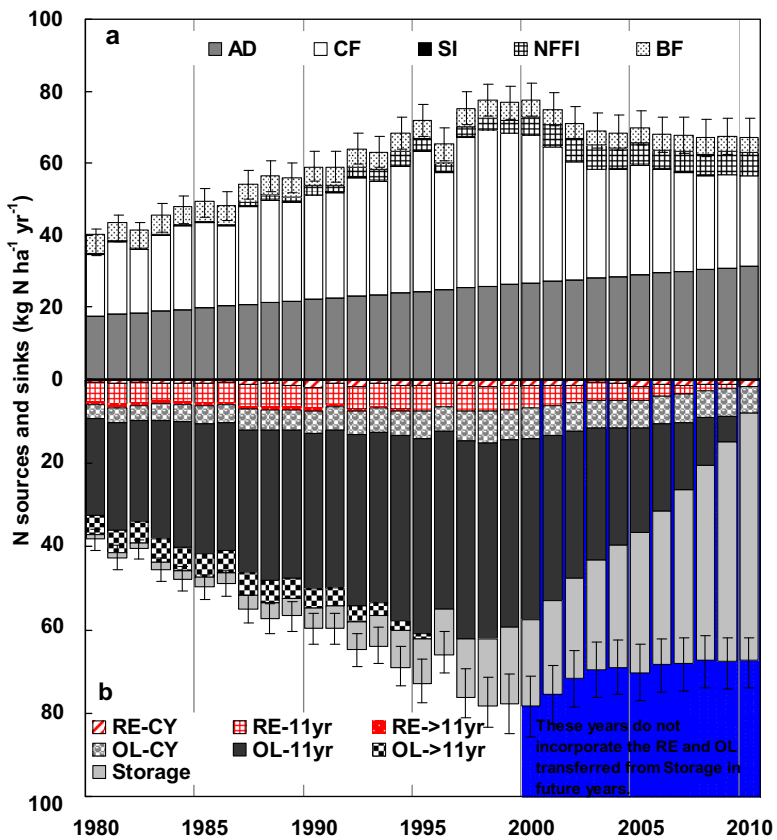

Figure 4. Dynamic net anthropogenic N input sources (a) from atmospheric deposition (AD), chemical fertilizer (CF), biological N fixation (BF), net food and feed input (NFFI), and seed input (SI) and sinks (b) for N exports by river from the current year (RE-CY), succeeding 1–11 years (RE-11 years), and succeeding 12–30 years (RE->11 years), other losses (OL, e.g., denitrification, nonharvested biomass uptake, and wood product export) from the current year (OL-CY), succeeding first 1–11 years (OL-11 years), and succeeding 12–30 years (OL->11 years), and net storage in watershed after 1–31 years (1980–2010) in the Yong'an River watershed. Error bars denote the 95% confidence interval of the fluxes. Note: The decreasing trends observed for cumulative RE and OL over the 2001−2010 period (as shown with blue shadow) result from their estimates using progressively fewer years (0–10 years) of the succeeding years' RE and OL data. With each passing year, the estimated net storage of annual NANI for years 2001–2010 will be decreased by increasing cumulative RE and OL fluxes.

only represented 1.7% (mean range: 1.1−2.5%) of the corresponding year's NANI. The majority of riverine export occurred in the succeeding 11 years, which represented 9.1% of the corresponding year's NANI. Estimated mean loss of annual NANI via denitrification, nonharvested biomass uptake and wood product export from the current year was 5.8 kg N ha^{-1} yr^{-1} (mean range: 3.4−7.6 kg N ha^{-1} yr^{-1}) (Figure 4b), which represented 9.2% (mean range: 8.7−10.7%) of the corresponding year's NANI. The majority of this loss occurred in the succeeding 11 years, which represented 41.8% of the corresponding year's NANI. Mean riverine N export (R^2=0.53, p<0.01) and loss via denitrification, biomass uptake and wood product export (R^2=0.75, p<0.01) of annual NANI from the current year showed increasing trends over the 1980−2010 period (Figure 4b). Over the 2000−2010 period, the decreasing trends observed for cumulative riverine export (decreasing from 6.9% of NANI in 2000 to 0% of NANI in 2010 with an average of 4.3%) and other losses (decreasing from 55.5% of NANI in 2000 to 0% of NAN in 2010 with an average of 32.7%) of annual NANI in the succeeding years resulted from their estimates only including exports and losses for the succeeding 0–10 years (rather than the entire ~11 years lag time due to the lack of future data to calculate riverine export and other loss pathways). This results in an increase of the estimated transient storage of annual NANI (increasing from 26.4% of NANI in 2000 to 88.3% of NANI in 2010 with an average of 51.8%). With each passing year, the estimated net storage of annual NANI for years 2001–2010 will decrease due to increasing cumulative riverine export and other losses transferred from the transient storage pool in future years (i.e., 2011–2021). If we use the mean β and θ values from 2000 to 2010 and project into the future (i.e., 2011−2021), on average 12.7% and 54.8% of the annual NANI for years 2000−2010 are predicted to be removed via riverine export and other losses in the succeeding 11−21 years, respectively, while only 21.3% of NANI is predicted to remain in the transient storage pool within the watershed. Over the 1980−2010 period, estimated mean transient storage of annual NANI in the watershed after 1−31 years was 16.8 kg N ha^{-1} yr^{-1} (mean range: 1.0−56.9 kg N ha^{-1} yr^{-1}) (Figure 4b), which represented 25.0% (mean range: 2.6−88.3%) of the corresponding year's NANI. Over the past 31 years, cumulative riverine export; losses via denitrification, nonharvested biomass uptake and wood product export; and transient storage represented ~13%; ~62%; and ~25% of total NANI, respectively.

3.3. The Transient Storage Legacy N Mass Dynamics

Using equations (3) and (14), in the Yong'an River watershed estimated mean transient storage of legacy N in landscapes (e.g., soil, groundwater and river sediment) increased from 380 kg N ha^{-1} yr^{-1} in 1980 to 534 kg N ha^{-1} yr^{-1} in 2010, suggesting a net increase of 154 kg N ha^{-1} yr^{-1} or 44% over the past 31 years (Figure 5). The residual anthropogenic N inputs prior to 1980 (i.e., the initial storage of legacy N mass observed in 1980, which is estimated from equation (14)) represented ~28% of annual transient N storage in the watershed on average, while new residual NANI represented ~72% over the 1980–2010 study period. Due to losses via riverine export, denitrification, nonharvested biomass uptake and wood product export, the residual transiently stored N in 1980 decreased with time to 11.5 kg N ha^{-1} yr^{-1} in 2010. Therefore, >50% of the stored legacy N mass was derived from new NANI during the study period since 1986.

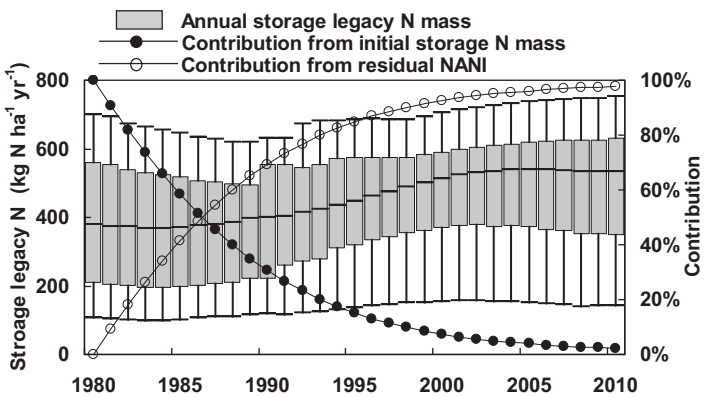

Figure 5. Dynamic transient storage of legacy nitrogen mass (box plots) and the contributions of the initial storage mass in 1980 (i.e., residual anthropogenic nitrogen prior to 1980, open circles) and residual NANI (fill circles) over the 1980–2010 period. Box plot denotes 97.5, 75, 50, 25, and 2.5% confidence interval for estimated legacy N mass.

3.4. Riverine TN Source Apportionment

In the Yong'an River watershed, estimated mean natural background sources contributed ~1.4 kg N ha^{-1} yr^{-1} (mean range: 0.7–2.3 kg N ha^{-1} yr^{-1}) and represented ~13.0% (mean range: 8.1–16.5%) of the observed annual riverine TN export over the 1980−2010 period. Current year's NANI only contributed

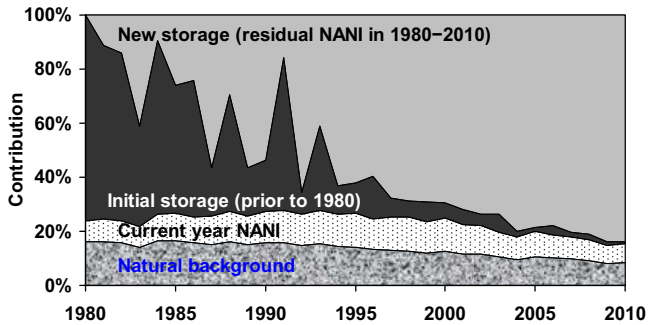

Figure 6. The contributions of current year net anthropogenic nitrogen inputs (NANI), previous year NANI (new storage N mass), initial legacy N storage (residual anthropogenic nitrogen prior to 1980), and natural background sources to observed annual riverine TN export in 1980−2010 in the Yong'an River watershed.

~1.1 kg N ha^{-1} yr^{-1} (mean range: 0.6–1.7 kg N ha^{-1} yr^{-1}) and ~10.0% (mean range: 6.8–12.6%) of annual riverine TN flux (Figure 6). The residual previous years' NANI (i.e., new storage) contributed ~6.5 kg N ha^{-1} yr^{-1} (mean range: 0–18.9 kg N ha^{-1} yr^{-1}) and ~55.0% (mean range: 0–84%) of annual riverine TN flux (Figure 6), while the initial transiently stored legacy N mass (observed in 1980, Figure 5) contributed ~1.9 kg N ha^{-1} yr^{-1} (mean range: 0.2–5.6 kg N ha^{-1} yr^{-1}) and ~22.0% (mean range: 0.1–76%). Therefore, the transiently stored legacy N from previous years represented ~77% of annual riverine TN flux. Of cumulative riverine TN flux, ~65% originated from NANI in 1980−2010.

4. Discussion

4.1. Efficiency of the Dynamic Watershed N Delivery Model

Bayesian calibrated coefficients a_i, b_j, and C_b for the dynamic watershed N delivery model that only considered annual water yield as the explanatory variable for β and average temperature for θ have small Monte Carlo errors (Table 2, <1% of standard deviation), indicating that the Bayesian model converged well [*Chen et al.*, 2013]. The modeled riverine TN fluxes closely matched LOADEST estimated values, as indicated by a high R^2 value and Nash-Sutcliffe coefficient (Figure 3a). These results are comparable with other watershed nitrogen simulations using mechanistic models (Nash-Sutcliffe coefficients >0.65 are considered very good, reviewed by *Moriasi et al.* [2007]), as well as lumped watershed models and statistical models developed between NANI and riverine TN flux (Nash-Sutcliffe coefficient commonly varied between 0.65 and 0.90 and R^2 varied between 0.70 and 0.95) [*Smith et al.*, 1997; *McIsaac et al.*, 2001; *de Wit et al.*, 2000; *Alexander et al.*, 2008; *Han et al.*, 2009; *Wellen et al.*, 2012; *Chen et al.*, 2013; *Wang et al.*, 2014]. The model residuals displayed constant variance and were independent of the magnitude of TN flux (Figure 3b), further indicating the robustness of the model [*Alexander et al.*, 2008]. Considering the complexities of N delivery across watershed landscapes, the modeled results are very reasonable, indicating the efficiency of the calibrated model for the Yong'an River watershed. Although this model, as well as other lumped watershed models, lacks the ability to predict seasonal or daily riverine N flux compared to mechanistic models, it is capable of quantifying the effects of transient storage on riverine N export and determining the dynamic fates of NANI over years.

Using the calibrated model, the mean natural background exports of 0.7–2.3 kg N ha^{-1} yr^{-1} were similar to estimates from several previous studies (i.e., 0.7–2.8 kg N ha^{-1} yr^{-1}) [*Han et al.*, 2009; *Howarth et al.*, 2012; *Swaney et al.*, 2012]. The estimated cumulative export fraction of NANI by the river in the current year and succeeding 1−30 years was ~13% (Figure 4b), which falls within the range of previous estimates (10–40%) for the export fraction of multiyear averaged NANI [*Schaefer and Alber*, 2007; *Han et al.*, 2009; *Schlesinger*, 2009; *Howarth et al.*, 2012; *Swaney et al.*, 2012], but is generally lower than the median value (~20%) for those watersheds. The lower export fraction in this study may be due to the lack of consideration for the transient storage effect in previous studies and the high N retention or assimilation capacity resulting from a high percentage of forests in this watershed (~67%, Figure 1). Estimated loss of NANI (~62%) via denitrification, nonharvested biomass uptake and wood product export was comparable with estimated results for 16 watersheds in the northeastern U.S.A (~65%) [*Van Breemen et al.*, 2002] and in Europe (50−90%) [*Vogt et al.*, 2013]. Assuming that ~15% of total NANI (or 33% of atmospheric N deposition) was removed by wood product export and forest biomass storage as observed in eastern China [*Sheng et al.*, 2014], denitrification would by difference account for the fate of ~47% of total NANI in the Yong'an River watershed. This denitrification percentage is similar to the sum of agricultural land denitrification (i.e., 36–48% of total N applied) [*Yan et al.*, 2011; *Ti et al.*, 2012; *Wang et al.*, 2014] and in-stream denitrification (i.e., 10–35% of total

N input to rivers) [*Yan et al*., 2011; *Chen et al*., 2013; *Wang et al*., 2014] in the surrounding region, as well as the 35–44% in soils and 11–20% in rivers estimated in global N budgets [*Seitzinger et al*., 2006; *Houlton and Bai*, 2009; *Groffman*, 2012; *Wang et al*., 2014]. These comparisons provide further support for the efficiency of the dynamic watershed N delivery model developed for the Yong'an River watershed.

4.2. Development of the Transient Storage (Legacy) N Pool

Two contributors to formation of the transiently stored N pool are the progressive N saturation of the watershed and the long residence time of N through the watershed (i.e., soils and aquifer/groundwater). In temperate watersheds, a threshold value of ~10.7 kg N ha^{-1} yr^{-1} has been suggested for N-saturation, above which significantly higher N fluxes in rivers were observed [*Howarth et al*., 2012; *Swaney et al*., 2012]. In forests of southern China, N losses increased dramatically as atmospheric deposition exceeded 10 kg N ha^{-1} yr^{-1} [*Fang et al*., 2009]. Observed NANI (38.0−77.6 kg N ha^{-1} yr^{-1}, Figure 4a) and atmospheric N deposition (17.5−31.3 kg N ha^{-1} yr^{-1}, Figure 4a) in the Yong'an River watershed far exceed these thresholds, suggesting that NANI likely exceeds the capacity of the terrestrial and aquatic ecosystems to assimilate N inputs. A national N mass balance study also showed that reactive N accumulated in Chinese terrestrial ecosystems increased from 7.9 to 17 Tg from 1978 to 2010, resulting in progressive N saturation of many ecosystems [*Cui et al*., 2013]. Due to progressive N saturation, the potential to assimilate new N additions is limited [*Cui et al*., 2013], resulting in increasing riverine export and other losses (i.e., denitrification, nonharvested biomass uptake and wood product export) of annual NANI from current years ($p<0.01$, Figure 4b) and increasing transient storage in the watershed (Figure 5) from 1980 to 2010.

In the Yong'an River watershed, loss of annual NANI via river export (~13%) as well as denitrification, nonharvested biomass uptake and wood product export (~62%) occur in the current year and succeeding 30 years (Figure 4b). This result is consistent with a long-term field study conducted under rotating sugar beet and winter wheat cultivation near Châlons-en-Champagne (France) using a ^{15}N tracer that showed 8–12% of the applied ^{15}N fertilizer was exported to the hydrosphere and >60% was removed by denitrification and biomass uptake in the succeeding 30 year period [*Sebilo et al*., 2013]. Furthermore, ~90% of the total loss over the 31 year study period occurred in the current and succeeding 11 years (Figure 3b), suggesting that there is at least a 12 year residence time for N in the watershed. This estimated N residence time is supported by trends in annual mean TN concentration/flux and flow-adjusted nitrate concentrations (nitrate represented 55% of measured TN in 1980–2010 on average) during the low flow (base flow) regime (70–100% flow duration interval, when discharge is mainly supplied by groundwater inputs) (Figure 3a and Figure 7a). Between 1980 and 1989, despite a 50% increase of NANI, riverine TN concentration/flux and base flow nitrate concentrations did not increase. Beginning in the early 1990s (~12 year lag), both of these riverine N species experienced increasing concentrations. This continuous increase of TN concentration/flux and nitrate concentrations continued through 2010, in spite of the 13% decline in NANI that was observed from 2000 to 2010. These riverine N dynamics support the decadal length lag effect between NANI and riverine N export resulting from transient N storage within the watershed.

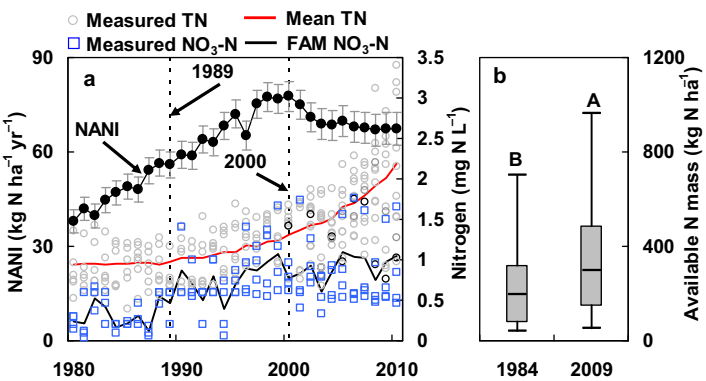

Figure 7. Responses of river TN concentration (n=250, red line denotes annual mean concentration estimated by LOADEST) and nitrate concentration (n=95, black line denotes flow-adjusted mean (FAM) concentration during the low flow regime (70–100th interval)) to (a) changes in NANI and (b) change in soil available nitrogen mass (n=195) in the upper 20 cm of agricultural soils between 1984 and 2009 in the Yong'an River watershed. Capital letters above bars denote significant differences ($p<0.01$). Error bars denote the 95% confidence interval of NANI. Box plot denotes 97.5, 75, 50, 25, and 2.5% confidence interval for soil available N content.

The residence time of N in watersheds is mainly dependent on hydrological and biogeochemical processes in the watershed [*Hamilton*, 2012]. As a result, if annual temperature was increased by 4% or annual water yield was increased by 20%, cumulative N loss (e.g., denitrification, nonharvested

Table 3. Sensitivity Analysis for Changes of Riverine Export, Other Losses (e.g., Denitrification, Nonharvested Biomass Uptake, and Wood Product Export), and Net Watershed Storage in Watershed Landscapes for Cumulative NANI Over the 1980–2010 Period in Response to Changes in Temperature, Water Yield, and Parameter θ in the Yong'an River Watershed[a]

Changes in Variables and Parameter		Changes in Various N Fates		
		Net Storage	Riverine Export	Other Losses
Temperature	+4%	−3%	−2%	+5%
	−4%	+5%	+3%	−5%
Water yield	+20%	−3%	+17%	−2%
	−20%	+3%	−16%	+3%
θ	+20%	−15%	−10%	+8%
	−20%	+19%	+9%	−7%

[a]Percentage changes for annual temperature (±4%) and water yield (±20%) are based on their coefficient of variances observed in 1980–2010.

biomass uptake and wood product export) and riverine export could increase by an estimated 5% and 17%, respectively (Table 3), and subsequently ~90% of the total loss of annual NANI would occur in the current and succeeding 8–9 year (e.g., N residence time of 9–10 years). Stable isotopic tracers (mainly ^{3}H) have shown that delivery times for surface runoff, soil water/shallow groundwater, and groundwater to river systems are on the order of months, years, and decades, respectively [*Sanford and Pope*, 2013; *Tesoriero et al*., 2013]. Similarly, incorporation of N into soil organic matter and subsequent release of this N for potential loss to the atmosphere, biomass, and hydrosphere is estimated to require several years to decades [*Mulvaney et al*., 2001; *Hamilton*, 2012; *Sebilo et al*., 2013]. Depending on hydrological conditions, the residence time for N deposited in sediments of rivers (<1 year) and reservoirs (several years) can further increase overall residence time within a watershed [*Han et al*., 2009; *Yan et al*., 2011]. The estimated ~12 year residence time for N in the Yong'an watershed, which is an integration of all these processes delaying N delivery from the watershed to the river, atmosphere, and biomass, might be reappeared in other regions with similar characteristics. Because of the decade long residence times for N in the watershed, surplus anthropogenic N input prior to 1980 represented a considerable contribution (~28% on average) to the annual transient storage of legacy N (Figure 5) and ~25% of the total NANI over the 1980–2010 period was transiently stored in the watershed (Figure 4b). This estimated storage fraction is coincident with the estimate that 16% of global anthropogenic N inputs are retained in the biosphere and groundwater [*Schlesinger*, 2009]. In terms of uncertainty, if the parameter θ incorporated a ±20% uncertainty (sensitivity analysis), net storage of total NANI over the 1980–2010 study would be overestimated by 19% or underestimated by 14% (Table 3), and subsequently N residence time would be increased to 14 years or decreased to 8 years. These results suggest that riverine TN export monitoring should be continued in the future to further verify the model results and to more rigorously identify the factors influencing N residence time.

Over the past 31 years, estimated annual transient storage of legacy N in soils, vadose zone, groundwater and river sediment increased by ~41% (Figure 5), further suggesting that the watershed biological assimilation capacity for N has become progressively saturated [*Howarth et al*., 2006; *Worrall et al*., 2009; *Swaney et al*., 2012]. This increasing transient storage of legacy N is consistent with the 105 kg N ha^{-1} of available net N accumulation (or a 65% increase of available soil N) between 1984 and 2009 observed in upper 20 cm layer of agricultural soils in the Yong'an River watershed (Figure 7b). Similar results also have been observed in 0–400 cm soil profiles in several typical agricultural lands (e.g., vegetables, fruits, and cereals) of China, i.e., 209–1776 kg N ha^{-1} of total nitrogen net accumulation after 3–16 years of continuous application of fertilizer N (110–900 kg N ha^{-1} yr^{-1}) [*Ju et al*., 2004], as well as the N enrichment observed in the 0–25 cm soil zone in the humid subtropical forests in southern China [*Zhang et al*., 2013]. Transient storage of legacy N in groundwater was also supported by the 2.7-fold increase of flow-adjusted nitrate concentration from 1980 to 2010 during the base flow period in the Yong'an River (Figure 7a). The considerable increase in base flow nitrate concentration and available N accumulation in soil profiles further highlight the role of soil and groundwater transient storage as contributing factors to long residence times for N in this watershed (Figure 4b).

4.3. Effect of the Transient Storage on Riverine TN Flux

Over the 1980–2010 study period, observed annual riverine TN flux in the Yong'an River was mainly derived from legacy N sources (~77%, Figure 6). This is consistent with results observed in field and watershed scale studies where 25−80% of annual N loss originated from mineralization of soil organic matter [*Booth et al*., 2005; *Kopáček et al*., 2013; *Chen et al*., 2014] and nitrate exported from groundwater or base flow accounted

for 30−40% of riverine nitrate flux [*Iqbal*, 2002; *Puckett et al*., 2011; *Sanford and Pope*, 2013]. These results stress the need to consider the transient storage effect in watershed models to better understand and simulate N delivery lag times that are often observed between changes in N inputs to watersheds and changes in riverine N export [*McIsaac et al*., 2001; *Meals et al*., 2010; *Swaney et al*., 2012; *Bouraoui and Grizzetti*, 2014]. Due to the transient storage effect, changes in NANI take at least 12 years (current year plus succeeding 11 years) to be fully realized (>90%) in terms of riverine N flux (Figure 4b). Therefore, a 12 year moving average for NANI would be appropriate for predicting annual riverine N export for lumped watershed models in the Yong'an River watershed, as well as in other watersheds with similar characteristics. For watershed mechanistic models, an appropriate model calibration should contain at least a 12 year continuous data record to effectively represent changes in riverine N flux in response to changes in N inputs. These findings are consistent with *Howden et al*. [2011], who suggested that a monitoring period of ≥12 years is required to fully determine the response of river N fluxes to watershed management measures in model calibration. Of course, differences in climate, hydrology, soils, geology, land use, etc. will result in differences in transient storage effects among contrasting watersheds.

Given the size of the transient N storage pool estimated for 2010 (∼534 kg N ha^{-1} yr^{-1}, Figure 5), as well as the long residence time for N transport through the watershed (Figure 4b), it is expected that the riverine TN flux would remain elevated for at least 12 years (i.e., 2011−2022) even with no significant increase in NANI. If we use the mean β and θ values in 1980−2010, the transient N storage mass is predicted to yield 2.5−8.1 kg N ha^{-1} yr^{-1} of riverine flux as well as 10.2−50.5 kg N ha^{-1} yr^{-1} of loss flux to the atmosphere and biomass in 2011−2022, assuming no change in NANI. This prediction suggests that the effect of NANI reduction can be expected to take at least 12 years to reach its cumulative effect in terms of riverine TN export. Similar results have been observed in many American and European watersheds, where river N concentrations and fluxes continued to increase despite reductions of N inputs for one or more decades [*Albiac*, 2009; *Worrall et al*., 2009; *Dubrovsky and Hamilton*, 2010; *Meals et al*., 2010; *Argerich et al*., 2013]. Also, time delays on the order of 7−30 years have been observed in response to agricultural mitigation practices decreasing groundwater nitrate concentrations in American and European watersheds [*Puckett et al*., 2011; *Sanford and Pope*, 2013; *Bouraoui and Grizzetti*, 2014]. These findings emphasize that increasing trends for riverine N fluxes in N saturated landscapes of the world result from both current and legacy activities over the past decades [*Tesoriero et al*., 2013]. It is thus important to consider the time delay resulting from transient storage of legacy anthropogenic N in watersheds when developing and evaluating aquatic N pollution mitigation or restoration measures. Expectations for rapid improvements from nonpoint source pollution remediation efforts must be tempered as these efforts will likely require decades to be fully realized.

4.4. Uncertainty Implications for the Dynamic Watershed N Delivery Model

Since the model calibration procedure is based on the agreement with observed annual riverine N export, caution should be paid to the modeled N loss/retention via denitrification, nonharvested biomass uptake and wood product export, as well as the transient N storage mass even though the calibration performance was reasonable. Due to the inverse relationship between the proportions of N lost/retained via denitrification, nonharvested biomass uptake and wood product export and the transiently stored N, the transient storage of legacy N mass would be overestimated if N loss was underestimated (and vice versa). For example, if parameter θ was overestimated by 20%, N loss/retention via denitrification, nonharvested biomass uptake and wood product export would be overestimated by 8%, while the transient storage of residual NANI would be underestimated by 15% (Table 3). However, it is not possible to verify these model results by direct observations due to the unavailability of reliable and efficient approaches for measuring these parameters at the large watershed scale. Long-term records for changes in soil and groundwater N levels, denitrification across different watershed landscapes, forest biomass N storage, and wood product export quantity are required to indirectly verify the model results. Direct measurements of ^{17}O, ^{18}O, and ^{15}N isotopes [*Michalski et al*., 2004; *Gardner and Drinkwater*, 2009] as well as ^{3}H isotope [*Sanford and Pope*, 2013; *Tesoriero et al*., 2013] can be used to estimate riverine N sources and the ages of groundwater and surface water could also contribute to verifying model results. The model might be further improved by separating parameter θ into two parameters to individually specify the denitrification and nonharvested biomass uptake processes. The model calibration procedure for denitrification and nonharvested biomass uptake processes might be improved through consideration of other influencing factors as explanatory variables,

such as soil and sediment carbon contents [*Gardner and Drinkwater*, 2009] and vegetation index [*Smith et al*., 1997].

The developed dynamic watershed N delivery model is also subjected to the uncertainty derived from the assumption that annual new NANI and legacy N in transient storage would experience the same fate. With increasing NANI, more legacy N might be distributed into subsurface soils, vadose zone, and groundwater, while new added NANI might be retained in the surface soils and sediments, resulting in a potential difference in hydrological drivers influencing new NANI versus legacy N export to rivers. Therefore, the model might be improved by distinguishing separate runoff components (e.g., surface runoff, subsurface flow, and groundwater recharge indices or base flow) as explanatory variables for parameterization of β, considering the differences in transient times among groundwater (decades), surface runoff (days to months), and soil water (months to years) [*de Wit et al*., 2000; *Puckett et al*., 2011; *Sanford and Pope*, 2013; *Tesoriero et al*., 2013]. The assumption of first-order reaction dynamics to describe both N exported by river and N lost/retained via denitrification, nonharvested biomass uptake and wood product export also might be inefficient in matching the complexities of N transport and transformation processes. For example, modeling instream N denitrification efficiency and N export rate using a first-order reaction generally presented greater uncertainties in the higher flow regime and in land use with greater human disturbance, respectively [*Chen et al*., 2012]. Due to limited information available in previous studies, the prior distribution for each of the three unknown coefficients a_i, b_j, and C_b (they are used to parameterize β and θ) was assumed to follow normal distributions for Bayesian calibration, which might not fully reflect the reality and therefore require more quantitative knowledge for improvement in future studies. The transient storage of legacy N originates primarily from nonpoint sources [*Meal et al*., 2010]; thus the model could be further refined through distinguishing point source versus nonpoint source model inputs.

5. Conclusion

This study developed a dynamic watershed N delivery model to quantify the transient storage of legacy N mass, its contribution to riverine N flux, and the fate of annual anthropogenic N input over time. The efficacy of the model was demonstrated with a 31 year record of TN fluxes from the Yong'an River watershed. For the 31 year cumulative net anthropogenic N input record, ~25% and ~13% was stored in the watershed and exported by the river system, respectively, while ~62% was lost/retained by denitrification, nonharvested biomass storage and wood product export. Estimated transient storage of legacy N mass increased by ~154 kg N ha^{-1} yr^{-1} (~41%) between 1980 and 2010. The contribution of legacy N stored in the watershed in 2010 to riverine export and removal mechanisms (e.g., denitrification, nonharvested biomass uptake and wood product export) will continue for at least 12 years. The annual riverine TN flux was mainly derived from the legacy N pool (~77%), while the current year anthropogenic input N (~10%) and natural background sources (~13%) represented lesser contributions. These results emphasize the need to consider the effects of transient storage in improving current watershed N models, as well as for developing and evaluating N pollution control measures.

The findings demonstrated by this dynamic watershed N delivery model are difficult to assess with most current watershed models, since they do not effectively incorporate transient storage effects. This model offers a simple and efficient tool for determining transient storage effects on riverine N flux in response to changes in anthropogenic N inputs to watersheds. However, cautions should be paid to potential uncertainty incorporated in the modeled N loss/retention via denitrification, nonharvested biomass uptake and wood product export, as well as transiently stored N mass. When applying this model, extensive information from the literature and direct measurements for the examined watershed, including changes of soil and groundwater N levels, denitrification and forest N uptake efficiencies, as well as riverine N sources and water (surface water and groundwater) ages, are needed to further verify the modeled results. In the future, the model might be improved by adopting various runoff components as explanatory variables, specifying net N inputs for different sources and landscapes as model inputs, and individually parameterizing N removal processes.

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