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A modification of the Regional Nutrient Management model (ReNuMa) to identify long-term changes in riverine nitrogen sources

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ABSTRACT

Source apportionment is critical for guiding development of efficient watershed nitrogen (N) pollution control measures. The ReNuMa (Regional Nutrient Management) model, a semi-empirical, semi-process-oriented model with modest data requirements, has been widely used for riverine N source apportionment. However, the ReNuMa model contains limitations for addressing long-term N dynamics by ignoring temporal changes in atmospheric N deposition rates and N-leaching lag effects. This work modified the ReNuMa model by revising the source code to allow yearly changes in atmospheric N deposition and incorporation of N-leaching lag effects into N transport processes. The appropriate N-leaching lag time was determined from cross-correlation analysis between annual watershed individual N source inputs and riverine N export. Accuracy of the modified ReNuMa model was demonstrated through analysis of a 31-year water quality record (1980–2010) from the Yongan watershed in eastern China. The revisions considerably improved the accuracy (Nash-Sutcliff coefficient increased by ~0.2) of the modified ReNuMa model for predicting riverine N loads. The modified model explicitly identified annual and seasonal changes in contributions of various N sources (i.e., point vs. nonpoint source, surface runoff vs. groundwater) to riverine N loads as well as the fate of watershed anthropogenic N inputs. Model results were consistent with previously modeled or observed lag time length as well as changes in riverine chloride and nitrate concentrations during the low-flow regime and available N levels in agricultural soils of this watershed. The modified ReNuMa model is applicable for addressing long-term changes in riverine N sources, providing decision-makers with critical information for guiding watershed N pollution control strategies.

1. Introduction

Increasing anthropogenic nitrogen (N) inputs have substantially elevated riverine N loads worldwide, resulting in degradation of aquatic ecosystem health, impaired water quality for some beneficial uses, and eutrophication and hypoxia in many coastal ecosystems (Galloway et al., 2008; Howarth et al., 2012). To control N pollution effectively, quantitative assessment and identification of riverine N sources are required for optimizing pollution control strategies at the watershed scale.

Many lumped (e.g., export coefficient models, SPARROW, and PolFlow) and mechanistic models (e.g., AGNPS, HSPF, and SWAT) (De Wit et al., 2000; Moriasiet al., 2007; Li et al., 2015; Du et al., 2014) are available for quantifying riverine N sources. Although potentially more accurate results are obtainable from mechanistic watershed models, a major limitation is their requirement for a large amount of input data for calibration/validation of a given watershed making their application difficult and labor intensive for the large number of watersheds requiring assessment (Shrestha et al., 2008; Shen and Zhao, 2010; Chen et al., 2013). In contrast, export coefficient and statistical models require fewer data inputs but are limited by their annual time step, which makes it difficult to infer seasonal patterns of nutrient delivery (Chen et al., 2013). Such seasonal resolution is required to determine nutrient sources and loads during the most sensitive times of the year (e.g., typically the summer growing season) when eutrophication/hypoxia is most likely to occur in downstream water bodies (May et al., 2001; Bowes et al., 2009). The ReNuMa (Regional Nutrient Management) model, a semi-empirical and semi-process-oriented watershed model with modest and easily acquired data requirements (e.g., precipitation, temperature, land-use data, point source load, fertilizer and manure loads), provides an attractive alternative for addressing seasonal nutrient dynamics with acceptable accuracy (Hong and Swaney, 2013).

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Due to its attributes, the ReNuMa model has been widely applied for simulating temporal variations of river discharge and riverine nutrient sources in a range of watersheds with contrasting climate, geology and land use (Brandmeyer et al., 2007; Woodbury et al., 2008; Liu et al., 2012; Xie, 2012; Sha et al., 2013, 2014; Huang, 2014; Li et al., 2014; Lu et al., 2014). These previous studies using ReNuMa were successfully validated for N dynamics at relatively short-time scales (< 10 years). In contrast, long-term studies are necessary for exploring drivers and trends in riverine N pollution (Chen et al., 2014), since management decisions made on short-term data sets (even up to 15 years) could be misleading (Burt et al., 2008) and temporal fluctuations caused by climatic variation may be misinterpreted as resulting from human activities (Howden et al., 2011). With respect to the ReNuMa model, challenges exist in addressing long-term watershed N dynamics (Sha et al., 2013) related to the steady-state assumptions for atmospheric N deposition and transient storage of N in soils and aquifers.

Over longer time periods (several decades), atmospheric N deposition in a given watershed or region may experience large changes due to changing human activities. For example, a steady decline (~41% decline) in atmospheric N deposition from 1990 to 2010 was observed in many American regions due to effective controls on NO_x emissions (Davidson et al., 2011; Ellis et al., 2013). In contrast, a dramatic increase of N deposition (~60% increase) occurred in many regions in China (especially southeastern China, ~170% increase) from 1980 to 2010 due to rapid increases in consumption of fossil fuels and fertilizers (Liu et al., 2013). Previous studies of watershed N dynamics also indicate long transit times for N passing through soils, vadose zone and groundwater to surface waters (Meals et al., 2010; Sanford and Pope, 2013; Sebilo et al., 2013; Bouraoui and Grizzetti, 2014; Van Meter et al., 2017; Chen et al., 2018). This N transport lag time (i.e., time elapsed between watershed N inputs and riverine N export) can range from several years to decades (Meals et al., 2010; Hamilton, 2012; Chen et al., 2015b), implying that a considerable proportion of the current riverine N load may be derived from legacy N inputs (Chen et al., 2018; Van Meter et al., 2017). Therefore, the assumption of steady-state atmospheric N deposition inputs and transient storage of N in soils and aquifers in the ReNuMa model could introduce considerable uncertainty in addressing long-term changes in riverine N sources.

This study is the first attempt to address long-term (three decades) watershed-scale N dynamics using a version of the ReNuMa model that was modified to consider yearly changes in atmospheric N input and N-leaching lag effects with minimal additional data requirements. The model source code was revised to incorporate monthly changes in atmospheric N deposition rates over the entire study period. A cross-correlation analysis was adopted to determine the appropriate length of the multi-year period that should be used to estimate average nonpoint source N inputs to satisfy the steady-state assumption for predicting riverine N export. The accuracy of the modified model was assessed through analysis of a 31-year record (1980–2010) of riverine total N (TN) loads from the Yongan River watershed in eastern China, an area experiencing rapid economic development over the study period. The modified model retains the merits but overcomes selected limitations of the original ReNuMa model, providing decision-makers with a tool for informed management and mitigation of N pollution at the watershed scale.

2. Materials and methods

2.1. Study area

The Yongan River watershed is a representative mesoscale watershed (2474 km^2) in southeastern China that has experienced dramatic changes in N deposition and anthropogenic activities in the past three decades. The Yongan River is the third largest river of Zhejiang province and flows to the East China Sea (Fig. 1). The East China Sea coastal zone, downstream of the Yongan watershed, is a frequent region for eutrophication during May to October (Chen et al., 2007). The climate is subtropical monsoon having an average annual temperature of 17.4 °C and average annual precipitation of 1400 mm (Fig. 2a). The rainfall mainly occurs in May–October with a typhoon season occurring in July–September. The May–October period is considered the primary growing season, which is the most active period for agricultural activities. Total population within the watershed increased from ~590,000 to ~740,000 between 1980 and 2010. Over the 31-year study period, domestic livestock production (pig, cow, sheep and rabbit) decreased by ~25%, while poultry production (chicken and duck) increased 4.8-fold (Chen et al., 2015b). Agricultural land (including paddy field, garden plot and dry land, Table S1) averaged ~12% of total watershed area in 1980–2010 (Fig. 2b), with developed lands, forest, and barren land (including surface waters, wetlands, rock, and wildlands) contributing ~3, ~67, and ~18%, respectively. 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 since 2000 (Fig. 2c). The agricultural land area irrigated and drained with cement channels and pipes increased by ~2-fold since 2000 (Supplementary materials, Part A, 1).

2.2. Data preparation

Data inputs for the ReNuMa model include a series of parameter values and watershed monitoring data. Annual and seasonal riverine TN loads were estimated by LOADEST based on discrete TN concentration and daily river water discharge monitoring data (Supplementary materials, Part A, 2). Daily average temperature and precipitation were averaged from three monitoring stations located within the watershed (Fig. 1). Due to the high seasonal dependence of water discharge (Fig. 2a) and nutrient inputs, this study split the year into growing (May–October) and dormant (November–April) seasons. Land use (Fig. 2b) and population data for the 1980–2010 period were derived from local government yearbooks of Xianju County and Linhai City. Monthly nitrogen input data from various sources were processed to meet the model requirements (Table 1). Atmospheric deposition was obtained from annual average N deposition records reported for southeast China in 1980–2010 (Liu et al., 2013) and N emissions from crop residue burning were subtracted. These net atmospheric N deposition values were multiplied by a precipitation normalization index to obtain the slope and intercept for N deposition. Annual chemical and organic fertilizer N inputs were estimated by the applied amount of each fertilizer type and corresponding N content, and further divided by the area of agricultural land-use types to acquire the fertilizer application rate (kg-N ha^{-1} agricultural area yr^{-1}). Fertilizer application was assumed to occur in March as only the annual totals affect the dissolved N concentrations in the current model formulation. Manure application was processed in the same manner as fertilizer application. Monthly agricultural biological N fixation was based on data from a nearby region, which specified different N fixation percentages for different months (Li et al., 2014). Point source nutrient loads were estimated as the sum of domestic and industrial sources, and divided by 12 to obtain monthly point-source N loads (Table 1; Supplementary materials, Part A, 3).

2.3. The ReNuMa model framework and modifications

The ReNuMa model, a hydrologically-driven, quasi-empirical model is designed to estimate nutrient loads in mesoscale watersheds (up to several thousand km^2). It is based on a large-catchment transport model (Generalized Watershed Loading Function model; Haith et al., 1996) and a nitrogen-budgeting approach that sums N contributions from net food and feed transport across watershed boundaries, atmospheric N deposition, fertilizer application (including manure), and nitrogen fixation within the watershed (Hong and Swaney, 2013). Output from the ReNuMa model summarizes N inputs from different sources (e.g.,

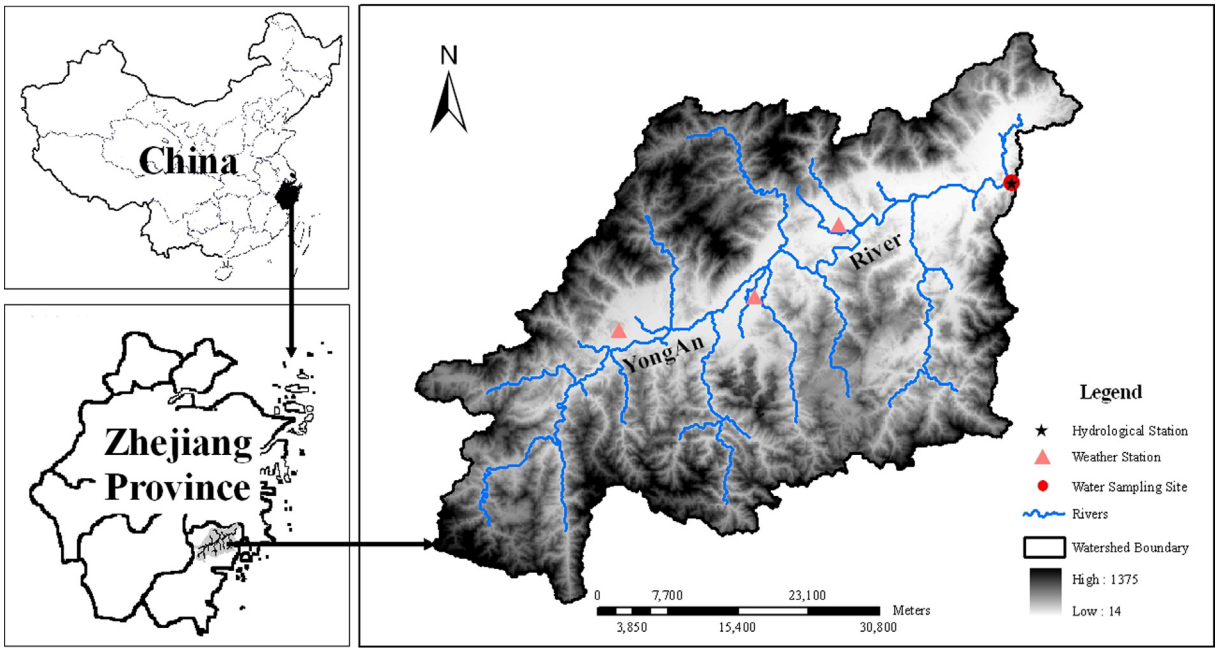

Fig. 1. Location of Yongan watershed in China and Zhejiang Province and the river hydrology and water quality sampling site.

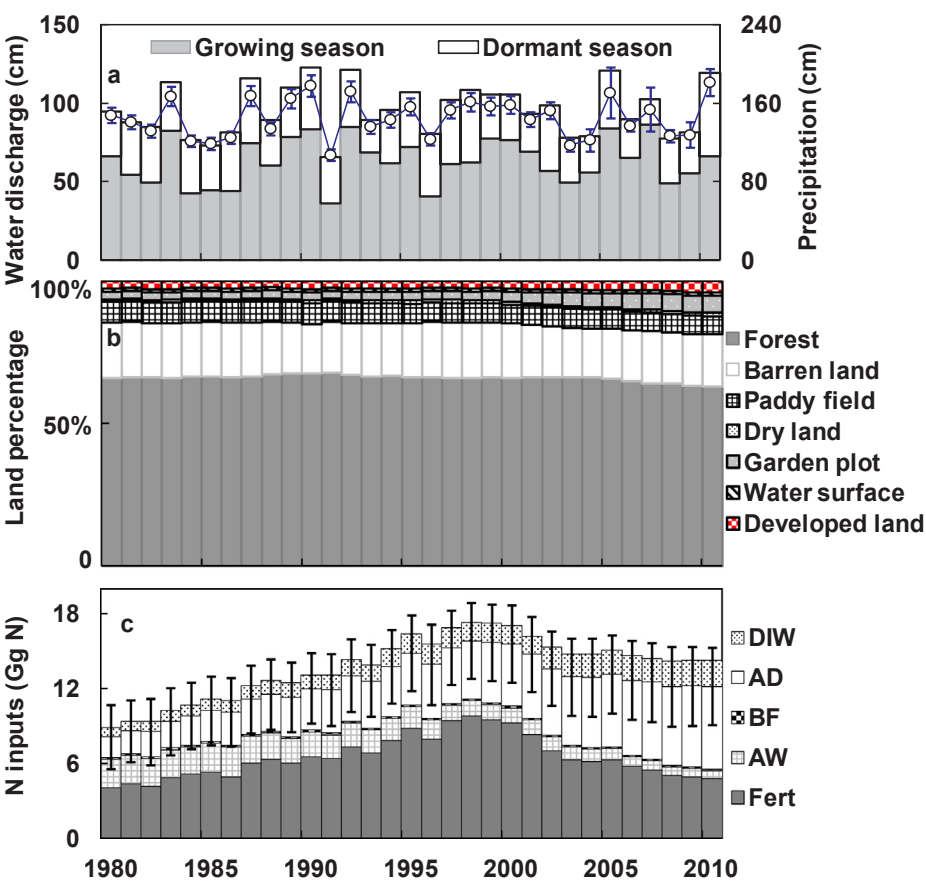

Fig. 2. Annual (a) river water discharge and precipitation, (b) land use, and (c) anthropogenic nitrogen inputs to the Yongan watershed in 1980–2010 (Human waste includes industrial and municipal point sources). DIW = domestic and industrial waste, AD = atmospheric deposition, BF = biological fixation, AW = animal waste, and Fert = fertilizer. Error bars in subfigure (a) refer to standard deviation of measurements from three weather monitoring sites within the watershed. Error bars in subfigure (c) denote the 95% confidence interval for total N inputs.

atmospheric N deposition, chemical fertilizer, animal waste, biological N fixation and domestic/industrial waste), estimates denitrification for aquatic processes, simulates total riverine N exports, and further divides N sources into point source, surface runoff and groundwater at annual and monthly time scales.

Watershed hydrological and erosion processes (Fig. S4a) are based on a lumped-parameter, watershed-scale hydrology and sediment transport model (GWLF model; Haith et al., 1996). The hydrological module of the ReNuMa model considers varying initial conditions, forcing functions (e.g. daily precipitation and a monthly ET cover factor) and human activities (i.e., land-use area variation) across different simulation periods (Hong and Swaney, 2013). Precipitation and

Table 1
Input N data sources and processing for the ReNuMa model.

Data type	Data source	Data processing
Atmospheric deposition	Original data were obtained from Liu et al. (2013) and the N emissions from crop residue burning were subtracted (Yan et al., 2011); then multiplied by the precipitation normalization index	Slope and intercept for atmospheric N deposition was summarized based on the data source
Chemical fertilizer	Annual nitrogen fertilizer (ammonium nitrate, ammonium bicarbonate, urea, and miscellaneous forms) application amounts in 1980–2010 were directly collected from the yearbooks	The fertilizer application (kg-N ha^{-1} agricultural area per year) was estimated by dividing by the area of agricultural land use types
Animal waste (manure)	Annual animal waste N input from human and livestock excreta was estimated by multiplying human and livestock population and the N excrement per human and livestock and the rate of excreta applied to field	The same as chemical fertilizer
Biological N fixation	Estimated based on the size of harvested area multiplied by average values for N fixed per unit area	Monthly agricultural N fixation apportionment is according to a relevant study conducted in nearby regions which specified different N fixation percentages for different months (Li et al., 2014)
Domestic and industrial waste (point source)	Domestic waste was estimated as the product of sewage concentration and domestic sewage discharge for urban and rural areas; Industrial source was estimated as the product of industrial wastewater discharge and the TN concentration in wastewater	According to field investigation, monthly domestic and industrial waste N load was equally distributed within a year

snowmelt are estimated from daily precipitation and temperature data. After removing water loss by evapotranspiration, a variation of the SCS (Soil Conservation Service) curve number is used to parameterize runoff from each land-use category. Water discharge consists of total watershed runoff from all source areas plus groundwater discharge from the unsaturated zone, shallow saturated zone and deep groundwater. Groundwater discharge is the product of groundwater recession constants and shallow saturated zone soil moisture contents. Partitioning of soil moisture into unsaturated, shallow saturated and deep saturated zones is similar to that used by Haan (1972). The USLE (Universal Soil Loss Equation) was used to generate watershed erosion (see Haith et al. (1996) for more detail).

When simulating biogeochemical processes (Fig. S4b), four general categories are included in the ReNuMa model: atmospheric N deposition, fertilizer application (including manure), nitrogen fixation and net nitrogen loads in food/feed across watershed boundaries. For consistency with the hydrological model, net food/feed transport across watershed boundaries was replaced by estimates of human sewage and septic system effluents and manure production in the current ReNuMa version. Riverine N loads from agricultural and forest lands resulting from nutrient inputs were calculated by a landscape response relationship (Eqs. S3 and S4) between N concentrations in runoff and groundwater and their hydrologic contributions to river water discharge. The atmospheric N deposition for non-agricultural and non-forested lands was regarded as a direct addition to streams. Domestic and industrial waste was assumed to be directly input to the river. Denitrification was considered in the transport of nitrogen from sources to riverine export along with hydrological processes (Fig. S4b) and was partitioned into runoff passing through landscapes, groundwater and in-stream components (Supplementary materials Part B, 1).

2.3.1. Incorporation of changing atmospheric N deposition

Considering the large variation of atmospheric N deposition over long time periods, the atmospheric N deposition accounting method was revised in the modified ReNuMa model to allow changes at the annual time step. We replaced the constant annual atmospheric N deposition load in the nutrient worksheet with two new parameters (i.e. the slope and intercept for the long-term annual N deposition equation; Fig. S5) in the source code, which allows the annual N deposition to change at an annual time step (see Supplementary materials Part B, 2.2).

2.3.2. Incorporation of nitrogen-leaching lag effect

The nitrogen-leaching lag effect is mainly associated with watershed hydrologic and biogeochemical processes (Sebilo et al., 2013; Chen et al., 2018; Van Meter et al., 2017). Previous studies (see Table 2) suggested that hydrological processes (e.g., surface runoff, evapotranspiration, groundwater recharge and discharge) and streamflow components (i.e., surface runoff vs groundwater) could be effectively simulated, implying that hydrologic or physical lag effects are at least partially accounted for in the ReNuMa model. To avoid overlap as well as reduce potential noise by high streamflow variability, cross-correlation analysis was introduced to identify the lag time between annual flow-adjusted riverine N concentration (i.e., streamflow independent N concentrations, see Supplementary materials Part A, 2) and anthropogenic N inputs (Chen et al., 2014). Once the appropriate lag time was determined from the data record, the annualized anthropogenic N input data were replaced with moving-average data to reflect the lag time. Cross-correlation analysis is a standard statistical method to measure correlation between two series of variables time-shifted against one another (Li et al., 2011). For example, let $Y = [Yt]$ be the time series of the dependent variable and $X = [Xt]$ be an independent time series. Assuming X and Y are jointly (annual) stationary, their cross-correlation is defined by $r_k(X,Y) = \mathrm{Corr}\ (Xt,Yt\text{-}k) = \mathrm{Corr}(Xt + k,Yt)$:

$$r_k(X,Y) = \frac{\sum_{t=1}^{n-k}(Y_t-\overline{Y})(x_{t+k}-\overline{X})}{\sqrt{\sum_{t=1}^{n}(Y_t-\overline{Y})^2}\sqrt{\sum_{t=1}^{n}(X_t-\overline{X})^2}}, k = 0,1,2... \quad (1)$$

where Y_t denotes annual flow-adjusted N concentration in the tth year, Y is the average flow-adjusted N concentration over the entire time series, X_t donates annual TN inputs in the tth year, X is average annual TN inputs over the entire time series, and k is an integer that denotes the lag interval. The procedures used in the cross-correlation analysis include (i) a prewhitening filter (AIC was chosen) was developed to remove autocorrelation from each N source time series; then, (ii) this same filter was applied to the concentration time series; and (iii) the N-leaching lag times between different N inputs and flow-adjusted riverine N concentration were assessed with cross-correlation analysis (Supplementary materials Part C, 2.1; Shumway and Stoffer, 2017). According to the lag times estimated by the cross-correlation analysis, we further updated the data inputs with the moving-average for each N input source.

2.4. Model calibration and validation procedures

Based on the two revised model components, a total of four versions of the ReNuMa model (Original ReNuMa V 2.2.2, ReNuMa V 2.2.2 + lag effect, ReNuMa V 2.2.2 New_Dep_Option, and ReNuMa V 2.2.2 New_Dep_Option + lag effect) were evaluated using the same Bayesian parameter estimation method and observations to estimate the effects of model modifications. Sensitivity analyses for both water discharge and TN were conducted to determine the most sensitive

Table 2
Summary of reported R^2 and Nash-coefficient (NS) values for modeling river water discharge and nitrogen flux in different watersheds by the ReNuMa model.

Variables	Calibration		Validation		Study area and modeled time period	Reference
	R^2	NS	R^2	NS		
Water discharge	0.79[a]	0.78[a]	0.76[a]	0.71[b]	YinMa He watershed (2006–2009)	Liu et al. (2012)
	0.79[a]	0.78[a]	0.63[c]	0.55[c]	Shitoumenkou reservoir watershed (2006–2009)	Xie (2012)
	0.92[a]	0.91[a]	0.94[a]	0.93[a]	Shuaishui Watershed (2000–2010)	Lu et al. (2014)
	0.88[a]	0.87[a]	0.82[a]	0.81[a]	Sha He River basin (1990–2001)	Sha et al. (2013)
	0.95[a]	0.94[a]	0.94[a]	0.93[a]	Lian River watershed (2003–2010)	Sha et al. (2014)
	0.92[a]	0.91[a]	0.99[a]	0.99[a]	Tangpu watershed (2009–2011)	Huang (2014)
	0.93[a]	0.90[a]	0.95[a]	0.95[a]	Tunxi catchment (2000–2010)	Li et al. (2014)
	0.82[a]	0.79[a]	0.82[a]	0.83[a]	Yongan watershed (1980–2010)	This study
DN	0.91[a]	0.90[a]	0.92[a]	0.90[a]	Shuaishui Watershed (2000–2010)	Lu et al. (2014)
	0.84[a]	0.74[b]	0.90[a]	0.54[c]	Sha He River basin (1990–2001)	Sha et al. (2013)
	0.94[a]	0.90[a]	0.96[a]	0.92[a]	Tunxi catchment (2000–2010)	Li et al. (2014)
TN	0.74[b]	0.70[b]	0.71[b]	0.66[b]	YinMa He watershed (2006–2009)	Liu et al. (2012)
	0.67[b]	0.76[a]	0.61[c]	0.55[c]	Shitoumenkou reservoir watershed (2006–2009)	Xie (2012)
	0.91[a]	0.90[a]	0.87[a]	0.86[a]	Lian River watershed (2003–2010)	Sha et al. (2014)
	0.84[a]	0.66[b]	0.95[a]	0.80[a]	Tangpu watershed (2009–2011)	Huang (2014)
	0.75[a]	0.58[c]	0.58[c]	0.51[c]	Yongan watershed (1980–2010)	This study (OM)
	0.75[a]	0.69[b]	0.64[c]	0.65[c]	Yongan watershed (1980–2010)	This study (LM)
	0.74[b]	0.74[b]	0.74[b]	0.74[b]	Yongan watershed (1980–2010)	This study (DM)
	0.74[b]	0.75[a]	0.75[a]	0.75[a]	Yongan watershed (1980–2010)	This study (DLM)

Superscript "a", "b" and "c" denote performance rating very good, good and satisfactory, respectively, as summarized by Moriasi et al. (2007); OM, LM, DM and DLM denote the original ReNuMa model (V 2.2.2), the model considering lag effect with fixed atmospheric N deposition rate, the model only considering annual changes in atmospheric N deposition, and the model considering changing atmospheric N deposition + lag effect, respectively.

model parameters. As no changes were made to the hydrological module, the Bayesian analysis was performed directly to acquire the best estimates for the most sensitive parameters and simulation results with the uncertainty ranges of water discharge. Based on the best estimates of water discharge, we further conducted the Bayesian analysis to obtain the most sensitive parameters and simulation results for TN. The 31-year data record for water discharge and TN were divided into two parts: the 1980–1999 period was used to acquire the best estimates for calibration of parameters and the 2000–2010 period was used for validation. The Nash-Sutcliff coefficient (NS) of model efficiency (Nash and Sutcliffe, 1970) and R^2 coefficient were used to evaluate goodness-of-fit for the monthly model predictions versus observed data. The standard deviation (STD) for modeled water discharge and TN was estimated in the Bayesian analysis.

Modified ReNuMa model outputs considering the lag effect and changing atmospheric N deposition were used to partition the TN export load originating from surface runoff, groundwater, and domestic/industrial sources. TN outputs were further divided into growing and dormant season periods to evaluate the highly contrasting differences in precipitation (Fig. S1), temperature, water discharge (Fig. 2a) and agricultural activities during the different seasons. ReNuMa model simulations were conducted in Microsoft Excel 2007. Cross-correlation analysis was conducted using EViews software (Ver. 6, Quantitative Micro Software, 2002). Goodness-of-fit with NS and R^2 was performed in MATLAB (Ver. 10.0, MathWorks Inc., Natick, MA, USA).

3. Results

3.1. Performance of the modified ReNuMa model

Sensitivity analysis for river discharge indicated that the "groundwater transfer coefficients for recession and seepage" were the most sensitive model parameters for the Yongan watershed (Table 3). Based on the sensitivity analysis, the most sensitive parameters for water discharge were calibrated with a Bayesian parameter estimation module. When compared to the literature (Table 2), the modified ReNuMa model performed well for river discharge dynamics (Fig. 3) within both the calibration ($R^2 = 0.82$, NS = 0.79) and validation ($R^2 = 0.82$, NS = 0.83) periods. Over the entire 31-year record, there was no significant changing trend in observed river discharge ($P > 0.05$). Model results indicated that groundwater (includes soil interflow, water from vadose zone and deep groundwater) contributed ~82% (73–91%) of water discharge, leaving ~18% (9–27%) originating from runoff. Contribution of groundwater to river discharge was lower during the growing season (May to October, mean: 66% (51–84%)) than the drier dormant season (November to April, mean: 88% (76–95%)) (Figs. 2a and 3).

Cross-correlation analysis indicated that annual riverine TN export load was not only related to nonpoint source N inputs during the current year, but also to nonpoint source N inputs from the previous 12 years (Fig. 4a). As expected, the lag time for point source N input was negligible (< 1 year). The analysis further indicated that the lag time for chemical fertilizer (~10 years, 4th–13th, Fig. 4b) was longer than that of manure and atmospheric N deposition (~9 years, 0th–8th, Fig. 4c and d), and was longer than that of N fixation (~8 years, 0th–7th, Fig. 4e). According to these distinct lag times, the moving-averages for N inputs were set as follows in the model input files: chemical fertilizer (4th–13th years), atmospheric N deposition (current and previous 8 years) and manure (current and previous 7 year), N fixation (previous 8 years), and point source N (current year).

For TN simulation, the most sensitive parameters were "slope", "slope increment" and "threshold" parameters relating agricultural N inputs to runoff N concentration, as well as the "threshold" parameters relating to forest runoff N concentration (Table 3). Nitrogen simulations for the four versions of the model showed significant improvement upon incorporation of a N-leaching lag time and annual changes in atmospheric N deposition inputs. A scatter plot examining monthly riverine TN load for the original versus modified models showed similar model results during the 1980–1990 and 1990–1999 periods, while simulated results for the 2000–2010 period were considerably underestimated by the original model due to ignoring the N-leaching lag effect and changes in atmospheric N deposition (Fig. 5a and b). Further, the model considering both the lag effect and annual changes in atmospheric N deposition inputs improved prediction accuracy more during the growing season, than the dormant season in the 1980–2010 period (Fig. 5c and d).

Compared to the original model, the models considering either the lag effect or variable atmospheric N deposition rates showed

Table 3
Parameter sensitivities and calibrated parameters for the ReNuMa model in the Yongan watershed.

Parameters	Subcategories	Parameter Sensitivities		Calibrated values			
		Upper	Lower	OM	LM	DM	DLM
Runoff curve number	Paddy field	0.0145	0.0078	80.3	80.3	80.3	80.3
	Orchards	0.0014	0.0010	60.7	60.7	60.7	60.7
	Forested land	0.0273	0.0199	71.2	71.2	71.2	71.2
	Dry land	0.0004	0.0003	59.8	59.8	59.8	59.8
	Open water	0.0000	0.0163	100.0	100.0	100.0	100.0
	Developed land	0.0217	0.0214	98.0	98.0	98.0	98.0
	Other land	0.0112	0.0078	68.2	68.2	68.2	68.2
Groundwater	Recession coefficient	0.1033	0.1230	0.123	0.123	0.123	0.123
	Seepage coefficient	0.1104	0.1133	0.037	0.037	0.037	0.037
	Denitrification fraction	0.4273	0.4273	0.398	0.399	0.405	0.405
Denitrification loss fraction	Paddy field	0.0672	0.0672	0.401	0.403	0.403	0.402
	Orchards	0.0133	0.0133	0.397	0.397	0.400	0.401
	Forested land	0.0755	0.0755	0.392	0.403	0.402	0.403
	Dry land	0.0037	0.0037	0.399	0.400	0.400	0.398
	Open water	0.0058	0.0058	0.398	0.401	0.402	0.403
	Developed land	0.0107	0.0107	0.399	0.399	0.399	0.400
	Other land	0.0213	0.0213	0.398	0.399	0.401	0.400
Agricultural class runoff N concentration	Intercept	0.0796	0.0796	1.548	1.523	1.502	1.507
	Slope	0.2075	0.2075	0.014	0.013	0.012	0.012
	Slope increment	0.4623	0.4623	0.020	0.025	0.022	0.025
	Threshold	0.5112	0.5112	161.9	159.9	180.6	173.6
Forest class runoff N concentration	Intercept	0.0053	0.0053	0.015	0.015	0.015	0.015
	Slope increment	0.0000	0.0000	0.20	0.20	0.20	0.20
	Threshold	0.0000	1.0461	19.7	20.0	18.8	21.6

The sensitivity is defined as the proportional change of variable y, relative to baseline yb, divided by the proportional change in parameter x, relative to baseline value xb. More details on sensitivity analysis are available in Supporting Information Part C 1. OM, LM, DM and DLM denotes the original ReNuMa model (V 2.2.2), the model considering lag effect with fixed atmospheric N deposition rate, the model only considering annual changes in atmospheric N deposition, and the model considering changing atmospheric N deposition + lag effect, respectively.

appreciable increases in the NS coefficient (Table 2). However, the model combining both the lag effect and annual changes in atmospheric N deposition inputs showed only a slight increase in the NS coefficient compared to the model only considering variable atmospheric deposition. This might be due to lack of data before 1980 for fully expressing the N-leaching lag effect and the large increase of atmospheric N deposition (~2-fold increase, Fig. S6) during the 1980–2010 period. When we replaced parameter values for the model only considering the lag effect with the calibrated parameters for the original model (Table 3), prediction accuracy for monthly riverine TN load was not significantly changed (R^2 = 0.75 and NS = 0.69 in calibration period; R^2 = 0.63 and NS = 0.65 in validation period). Similarly, the model considering both lag effect and variable atmospheric N deposition using the calibrated parameters from the original model yielded comparable accuracy for monthly riverine TN load (R^2 = 0.75 and NS = 0.69 in calibration period; R^2 = 0.74 and NS = 0.69 in validation period). These results suggest that setting the multi-year moving average for N inputs as well as considering variable atmospheric N deposition rates had a greater effect on prediction accuracy than the calibrated model parameters. As a result, the calibrated parameter values resulted in only limited changes among the four versions of the ReNuMa model examined in this study (Table 3).

3.2. Riverine N source apportionment

Based on the modified ReNuMa model that considered the lag effect and changing atmospheric N deposition, our results indicated that the annual riverine TN export load increased about 3-fold from 1640 ton N yr^{-1} in 1980 to 4987 ton N yr^{-1} in 2010, with a 31-yr average of 2773 ton N yr^{-1} in the Yongan watershed. Riverine TN load

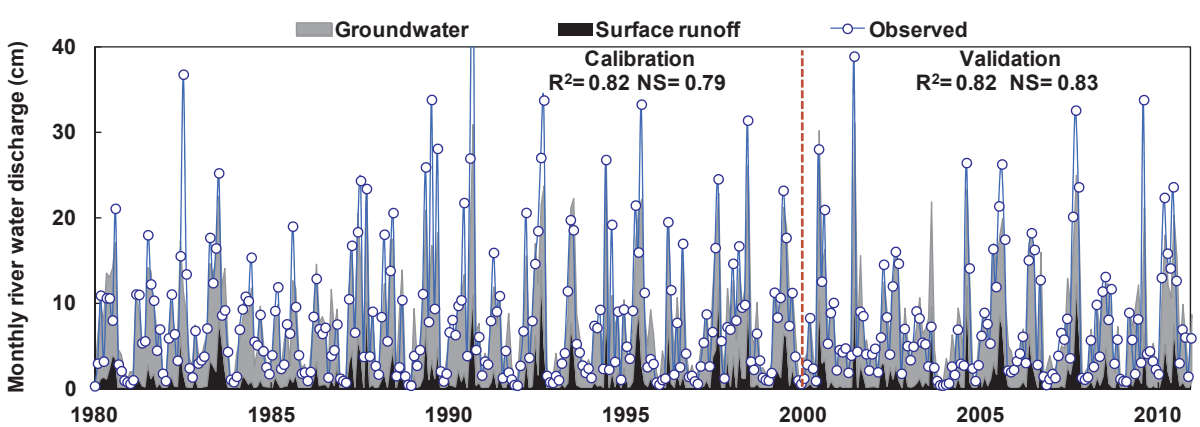

Fig. 3. Calibration and validation performances of the ReNuMa model for predicting river water discharge (groundwater + surface runoff) in the Yongan watershed over the 1980–2010 study period.

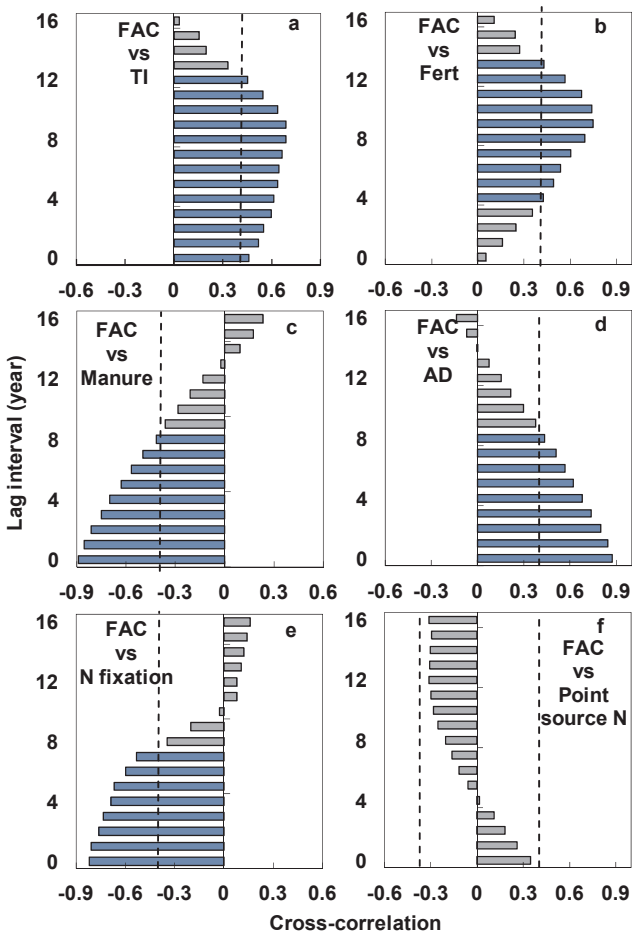

Fig. 4. Cross-correlations between annual flow-adjusted N concentration (FAC) and (a) total nonpoint source N input (TI), (b) fertilizer N application rate (Fert), (c) manure, (d) atmospheric N deposition (AD), (e) N fixation, and (f) point source N in the Yongan River watershed over the 1980–2010 period. Dashed perpendicular lines denote critical values for a $P < 0.05$ significance level. The blue bars identify the lag years. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

was divided into three components: surface runoff, groundwater, and domestic/industrial wastewater. The surface runoff N load increased from 332 ton N yr^{-1} in 1980 to 786 ton N yr^{-1} in 2010; however, the contribution percentage did not increase significantly ($P > 0.05$). Similarly, groundwater N load did not show an increased contribution to riverine TN export load (mean: ~67%; 58–81%, $P > 0.05$), but the groundwater N load increased more than 2-fold from 1285 ton N yr^{-1} in 1980 to 3376 ton N yr^{-1} in 2010. Riverine N load derived from domestic/industrial wastewater continuously increased from 23 ton N yr^{-1} in 1980 to 825 ton N yr^{-1} in 2010, representing a ~36-fold increase in over the past 31 years (Fig. 6a).

3.2.1. Point vs nonpoint sources

Nonpoint source N loads include surface runoff and groundwater inputs, and were considered to originate from atmospheric N deposition, fertilizer, animal waste and biological N fixation (Fig. 2c). In contrast, point source N loads were derived from domestic/industrial wastewater after wastewater treatment. Over the past 31 years, the nonpoint source N load (mean: 86%; 78–99%) dominated riverine TN source loading, while the point source N load provided a smaller (mean: 14%, 1–22%), but non-negligible contribution to the riverine TN load (Fig. 6a).

Due to seasonal changes in water discharge and nutrient inputs (Fig. 2a), seasonal point source and nonpoint source apportionment was further conducted to guide time-sensitive watershed management decisions. Nonpoint N sources generally contributed the majority of the TN load in both growing season (corresponding to high flow regime; mean: 89%; 79–99%; Fig. 6b) and dormant season (corresponding to low flow regime; mean: 80%; 6%–98%; Fig. 6c) between 1980 and 2010. Contributions of nonpoint N sources to the riverine N load were generally higher in the growing season than dormant season. The proportion and absolute mass of point source N increased appreciably during 1980–2010 for both growing and dormant seasons, with point source N (mean: 20%; 2–38%) contributions during the dormant season (Fig. 6c) being about twice as much as in the growing season (mean: 11%; 1–21%; Fig. 6b).

3.2.2. Surface runoff versus groundwater N sources

Due to the high proportion of nonpoint source N, we further divided the nonpoint N source into surface runoff and groundwater components (Fig. 6). Surface runoff N load was considered to originate from the current year's N inputs from several different sources, such as direct loading to streams from atmospheric N deposition, chemical fertilizer, animal waste, and biological N fixation (Fig. S4b). The groundwater N load mainly consists of legacy N sources associated with previous year's N additions from atmospheric N deposition, biological N fixation, animal waste and fertilizer leached to the saturated zone (Fig. S4b). For the entire 31-year period, groundwater dominated nonpoint source N loading (mean: 77%; 69–86%) with surface runoff contributing 23% (14–31%, Fig. 6a). As a result, groundwater contributed the major portion of riverine TN load and was comparable in both the growing (mean: 66%; 53–85%) and dormant (mean: 69%; 58–85%) seasons. In contrast, N in surface runoff contributed twice the percentage of riverine TN load during the growing season (mean: 23%; 7–34%) compared to the dormant season (mean: 11%; 3–24%). When comparing the results between growing and dormant seasons, groundwater contribution of nonpoint source N in the dormant season (mean: 86%; 73–95%) was higher than during the growing season (mean: 74%; 63–92%). The percentage of N from surface runoff was much higher during the growing season (Fig. 6b and c) due to higher rainfall/runoff during this season (Fig. 2a).

3.3. Fractional export of anthropogenic N inputs

In the Yongan watershed, the modified ReNuMa model that considered the lag effect and changing atmospheric N deposition estimated that watershed total point and nonpoint source N load delivery to the river continuously increased from 2652 ton N yr^{-1} in 1980 to 8269 ton N yr^{-1} in 2010. Modeled N removal due to aquatic denitrification (runoff + groundwater denitrification) increased from 1013 ton N yr^{-1} in 1980 to 3272 ton N yr^{-1} in 2010 and showed a significant positive relationship to temperature ($R^2 = 0.60$, $p < 0.001$, $n = 31$). Specifically, N removal by runoff denitrification (including instream denitrification) increased from 440 to 1274 ton N yr^{-1} between 1980 and 2010, while N removal by groundwater denitrification increased from 573 to 1998 ton N yr^{-1} between 1980 and 2010. There were no significant correlations between temperature and river water discharge ($p = 0.93$, $n = 31$), groundwater flow ($p = 0.54$, $n = 31$) and runoff ($p = 0.25$, $n = 31$), while significant correlations were observed between temperature and riverine TN load ($R^2 = 0.60$, $p < 0.001$, $n = 31$), surface runoff TN load ($R^2 = 0.43$, $p < 0.001$, $n = 31$) and groundwater TN load ($R^2 = 0.53$, $p < 0.001$, $n = 31$). These results imply that denitrification is more strongly regulated by temperature than hydrological processes. Fractional removal by aquatic denitrification varied from 38 to 40% during 1980–2010, which accounted for 9–18% of annual anthropogenic N input to the watershed (8900–18727 ton N yr^{-1}, Fig. 2c). As a result, N removal by aquatic denitrification accounted for 13% of cumulative anthropogenic N inputs to the watershed over the past 31 years (Table 4). In comparison,

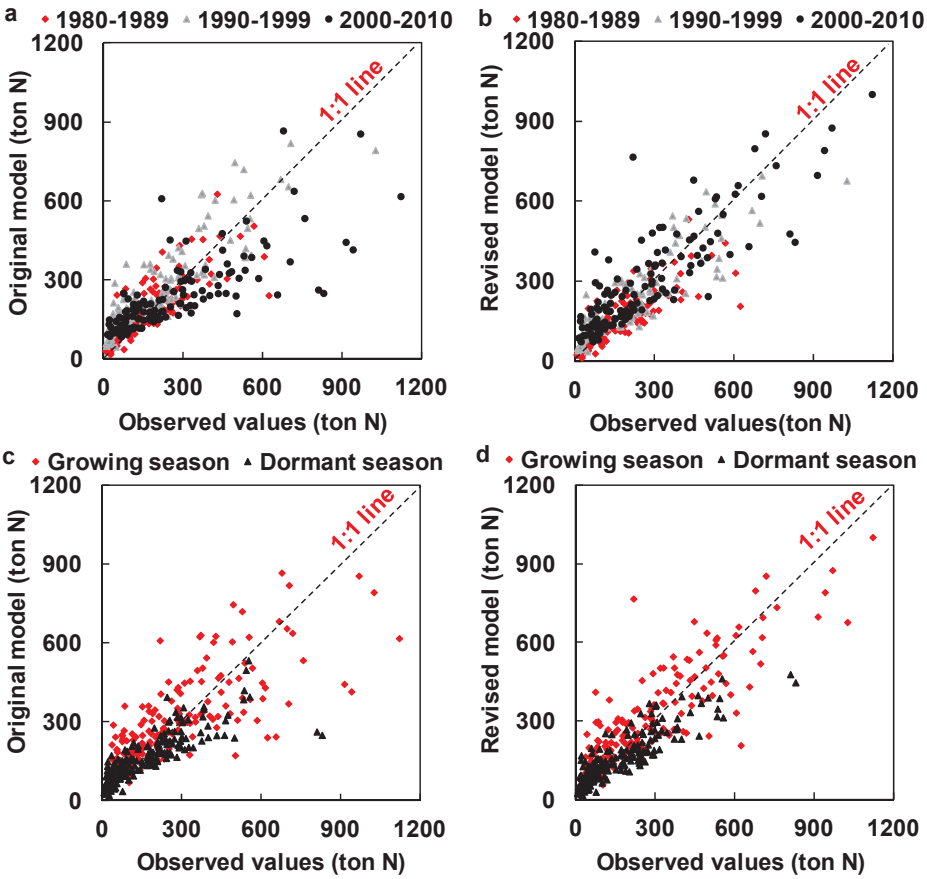

Fig. 5. Scatter plot for monthly riverine TN fluxes of observed versus (a) original model in different time periods, (b) revised model (ReNuMa V 2.2.2 New_Dep_Option + lag effect) in different time periods, (c) original model in two seasons, and (d) revised model in two seasons for the Yongan watershed over the 1980–2010 period.

the aquatic denitrification fraction of annual anthropogenic N input to the watershed estimated by the original ReNuMa model ranged from 9 to 14%. When focusing on the 2000–2010 period, the original ReNuMa model underestimated average aquatic denitrification by ~45% compared to the modified model that considered both the lag effect and changing atmospheric N deposition. By including aquatic denitrification, the estimated riverine export fraction of annual anthropogenic N inputs at the watershed outlet varied between 14 and 28%. The riverine export fraction estimated by the original ReNuMa model ranged from 16 to 25%. For the 2000–2010 period, the original ReNuMa model underestimated average riverine export fraction by ~15% compared to the modified model that considered both the lag effect and changing atmospheric N deposition. Based on estimated results from the modified ReNuMa model that considered the lag effect and changing atmospheric N deposition, riverine TN export accounted for 20% of cumulative anthropogenic N inputs to the watershed over the past 31 years (Table 4). The riverine export percentage of nonpoint source N inputs to the watershed (estimated as the ratio between annual riverine TN load and the 12-yr average nonpoint source N inputs to the watershed) ranged between 12 and 25% with an average of 17%. Fractional nonpoint source N exported by the river varied between 14 and 21% during 1980–2000 and increased from 15 to 25% in 2001–2010 ($P = 0.04$), which may mainly result from the ~2-fold increase in improved agricultural drainage area in the Yongan watershed since 2000.

4. Discussion

4.1. Reliability and efficacy of model modifications

Our modifications incorporating both the lag effect and changing atmospheric N deposition inputs considerably improved the accuracy of the ReNuMa model for predicting riverine N loads in the Yongan watershed in 1980–2010 (Table 2). No significant changes were observed in parameters values among the four versions of the ReNuMa model (Table 3) and higher prediction errors were found for the original model, especially during the growing season when eutrophication is most prevalent. These findings further highlight the importance of considering the N-leaching lag effect and variable atmospheric N deposition rates in predicting long-term riverine N export loads. The importance of considering the N-leaching lag effect and annual change in atmospheric N deposition was also well demonstrated by the considerable under-estimations of monthly riverine TN loads (Fig. 5) as well as the aquatic denitrification fraction and riverine export fraction by the original model for the 2000–2010 period. Although observed R^2 and NS values for riverine discharge and TN load simulations were not as high as some previous applications of the original ReNuMa model in different watersheds (Table 2), we believe the modified model provided better performance since the time scale of our study (31 years) was much longer than previous studies (< 10 years) and data before 1980 were unavailable for fully expressing the N-leaching lag effect. According to watershed model performance ratings (Moriasi et al., 2007), the modified model can be evaluated as "good" and "very good" during the calibration and validation periods, respectively (Table 2). In addition, estimated point-source contributions to riverine N loads increased ~37 times from 1980 to 2010 (Fig. 6a), consistent with the ~20 times increase in chloride concentration during the baseflow regime (70–100% flow duration interval, a proxy for wastewater inputs; Chen et al., 2016). Considering the complexities of N delivery at the watershed scale, the modeled results are very reasonable.

4.1.1. Role of lag effect

The N-leaching lag effect has been observed in various water bodies worldwide (Argerich et al., 2013; Bouraoui and Grizzetti, 2014; Van Meter et al., 2017). Cross-correlation analysis suggested the combined

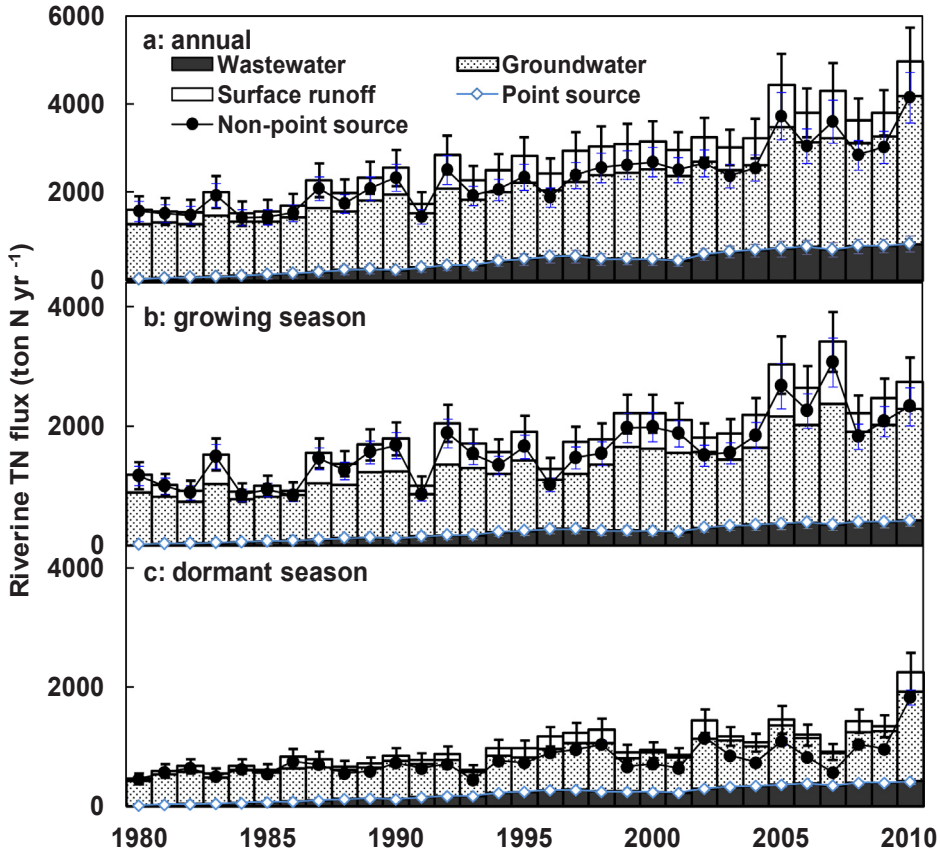

Fig. 6. Riverine TN fluxes derived from various sources for each year (a), growing season (b) and dormant season (c) in the Yongan watershed over the 1980–2010 study period. Error bars in subfigure (c) denote the 95% confidence interval of the N flux.

lag time between total nonpoint source N inputs (chemical fertilizer, manure, atmospheric N deposition and N fixation) and riverine export was as long as 13 years (Fig. 4a). This result is consistent with a decadal lag time previously determined between riverine TN export and anthropogenic N inputs in the Yongan watershed (Chen et al., 2015a; Chen et al., 2015b), as well as the 7–30 year lag times observed in other watersheds (McIsaac et al., 2001; Meals et al., 2010; Howden et al., 2011; Bouraoui and Grizzetti, 2014; Van Meter et al., 2017). The differences in lag times among various N sources determined by cross-correlation analysis (Fig. 4) are associated with specific features of each N source, such as proximity to streams, chemical nature of the input, and hydrologic and biogeochemical processing times (Chen et al., 2018). For example, a long-term field experiment indicated that a considerable proportion of applied chemical N fertilizer could be used by crops, transformed to soil organic N through degradation of litter and roots, and finally mineralized to nitrate for subsequent transport,

Table 4
Estimated cumulative nitrogen input-output balance in the Yongan watershed over the 1980–2010 period based on the modified ReNuMa model and reference sources.

N input (Gg N)		95% confidence interval
Atmospheric deposition	128.7 (30%)	87.6–167.2 (22–37%)
Chemical fertilizer	201.1 (47%)	167.1–254.9 (42–56%)
Animal waste	48.5 (12%)	30.0–63.7 (8–14%)
Biological N fixation	4.3 (1%)	3.2–5.3 (0.8–1.2%)
Domestic and industrial waste	43.6 (10%)	31.2–53.9 (8–12%)
Total	426.2	396.9–456.5
N output (Gg N)		
Riverine export	86.0 (20%)	73.0–98.9 (19–22%)
Aquatic denitrification	54.7 (13%)	39.3–69.1 (12–13%)
NH_3 volatilization	65.1 (16%)	50.3–81.6 (15–16%)
		Based on observations for croplands by Xing and Zhu (2000) and Zhao et al. (2009) and for human and animal wastes by Wang et al. (2009).
Forest biomass retention	29.1 (7%)	20.1–37.5 (6–7%)
		Based on observations by Sheng et al. (2014).
Denitrification in soils	101.6 (24%)	95.1–109.5 (21–28%)
		Based on observations by Gu et al. (2015) and Wang and Yan (2016).
Soils and groundwater storage	89.8 (20%)	60.1–125.8 (18–24%)
		Estimated as the balance
Total	426.2	337.9–522.4

resulting in a long residence time (decades) for N before leaching to groundwater (Sebilo et al., 2013). On the contrary, the lag effect for point source N pollution is negligible (Fig. 4f) due to short residence times (< 1 yr) for most point source N forms in the hydrologic system. Physically or biologically deposited N associated with sediments in a river system is subject to resuspension in future high-flow events as channels migrate laterally or as benthic communities die or are scoured (Chen et al., 2018).

The watershed N-leaching lag effect is mainly determined by hydrological and biogeochemical processes (Meals et al., 2010; Sebilo et al., 2013; Chen et al., 2014; Van Meter et al., 2017). Previous studies indicated that delivery times for soil water/shallow groundwater and deep groundwater to river systems ranged from years to decades (Sanford and Pope, 2013). Parameters associated with groundwater delivery were the most sensitive to water discharge (Table 3). Further, the considerable groundwater contributions to river discharge (82%, Fig. 3) and N load (67%, Fig. 6a) imply the potential for a considerable hydrologic lag effect due to groundwater delivery in the Yongan watershed. This premise is supported by a 2.7-fold increase in nitrate concentration in the baseflow regime (when discharge is mainly supplied by groundwater inputs) in the Yongan watershed (Chen et al., 2015a). Biogeochemical lag times result from the time necessary for incorporation of N within the root zone (likely in organic form) and its subsequent mineralization for potential NO_3^- leaching, which is estimated to require several years to decades (Sebilo et al., 2013; Van Meter et al., 2017). Support for the biogeochemical lag effect is demonstrated by the increase of 105 kg N ha^{-1} of net available N accumulation (a 65% increase of available soil N content) observed between 1984 and 2009 in the upper 20 cm layer of agricultural soils in the Yongan River watershed (Chen et al., 2015a).

Our results highlight the importance of the modifications made to the ReNuMa model for addressing long-term watershed N dynamics by considering the N-leaching lag effect. This study provides a first step toward incorporating the lag effect for estimating the appropriate length of the multi-year record required to realistically estimate average N inputs in the ReNuMa model by a simple cross-correlation analysis. However, such a multi-year moving-average approach partially obscures differences in N inputs among years within the lag time period and therefore requires further investigation to better incorporate the N-leaching lag effect into various models. To improve the model accuracy in this study, data prior to 1980 are required to match the estimated lag time lengths for fully expressing the N-leaching lag effect for the entire 1980–2010 study period. In addition to the requirements for a longer data record, further modifications to the hydrological and biogeochemical modules in the model may be warranted. Although the hydrologic lag effect has been at least partially considered in the hydrological module of the ReNuMa model as indicated by the high streamflow predictive ability in this study (Fig. 3), it may be beneficial to divide groundwater into more detailed components (e.g., vadose zone and groundwater) that would allow calculation of different residence times for distinct flowpaths with differing lag times for water and nutrients. For biogeochemical processes, modules that account for N storage and release dynamics in soils and vegetation would be beneficial to better characterize the N budget at the watershed scale. Mechanisms leading to intrinsic differences in lag time lengths for various N sources, as well as the contribution of N inputs from various years, require further refinement in both hydrological and biogeochemical modules. Due to the complexity of hydrological and biogeochemical dynamics in N delivery processes at the watershed scale, it is not currently possible to directly address lag effects for various N source input over long time periods. Thus, a statistical approach, such as the cross-correlation used in this study, using long-term hydrological and biogeochemical monitoring records across several contrasting systems is required to better understand N-leaching lag effects. This approach may be enhanced by direct measurements of multiple isotopes (e.g., ^{18}O and ^{15}N, ^{18}O and ^{2}H, and ^{3}H) and integration of multiple methods (e.g., conservative ions and heat tracers methods as well as relevant modeling methods). These integrated methods can be used for riverine N source apportionment, streamflow hydrograph separation, and age determination of groundwater and surface water (Sanford and Pope, 2013; Chen et al., 2015a), which contribute to elucidation of specific mechanisms and verify hydrological and biogeochemical lag effects for various N sources input across long time periods.

4.1.2. Role of increasing atmospheric N deposition

Large increases in atmospheric N deposition rates (i.e., increasing from 9.8 to 26.6 kg N $ha^{-1}yr^{-1}$ between 1980 and 2010) have been widely observed in southeast China in recent decades due to increasing N fertilizer use, domestic animals (major source of NH_3), and fossil fuel consumption (major source of NO_x) (Klimont et al., 2001; Liu et al., 2013). Such a rapidly increasing trend in N deposition would contribute to considerable uncertainty in simulation results if atmospheric N inputs were held at a constant value (Fig. 5). The dramatic increase of atmospheric N deposition (~2-fold increase) between 1980 and 2010 (Fig. S6) appears to have partially obscured the N-leaching lag effect. As a result, incorporation of the atmospheric N deposition modification provided a greater impact on model performance than that of incorporating the lag-time modification (Table 2). Sensitivity analysis (Table 3) showed that the "threshold" for forest runoff N concentration was one of the most sensitive parameters for the ReNuMa model. This suggests a threshold-type response to N deposition in forest lands (Eq. S4) and highlights the importance of considering the change in annual N deposition. Several studies have emphasized the importance of increasing N deposition which has led to N saturation in both non-agricultural and agricultural ecosystems and subsequently enhanced N loss to waters (Matson et al., 2002; Aber et al., 2003; Bobbink et al., 2010). Progressive N saturation is also evident in the one unit decrease in headwater stream pH concomitant with a 2.1-fold increase in riverine TN flux in forest catchments in the Yongan watershed since the 1990s (Chen et al., 2016). Therefore, temporal change in atmospheric N deposition should be incorporated into relevant models simulating long-term N dynamics at the watershed scale. Our model results may incorporate unavoidable uncertainty since the atmospheric N deposition data used in this study were adopted from observations in southeast China (Liu et al., 2013). To improve modeling accuracy, enhanced *in situ* monitoring for specific watersheds is warranted to identify long-term and seasonal changes in atmospheric N deposition for incorporation as model inputs.

4.2. Fate of anthropogenic N inputs

The modified ReNuMa Model results suggested that riverine TN export accounted for 20% of cumulative anthropogenic N inputs (point + nonpoint sources) at the Yongan watershed outlet over the past 31 years (Table 4). This estimate falls within the range of previous estimates (mean: 20%, 10–40%) for the export fraction of watershed anthropogenic N inputs by rivers worldwide (Schaefer and Alber, 2007; Han et al., 2009; Schlesinger, 2009; Howarth et al., 2012; Swaney et al., 2012; Van Meter et al., 2016). Model results indicated that aquatic denitrification cumulatively removed ~55 Gg N (Table 4) and accounted for 39% of the N load delivery to rivers (~13% of anthropogenic N inputs to the watershed) over the past 31 years. This estimate is consistent with results observed in the surrounding region (10–43% of total N input to rivers; Yan et al., 2011; Chen et al., 2013; Wang et al., 2014; Zhao et al., 2015). These comparisons provide further indirect support for the reliability of the model results in this study.

The estimated N imbalance of 285.5 Gg N (67%) between cumulative anthropogenic N input (426.2 Gg N) and riverine TN export (86.0 Gg N) and aquatic denitrification removal (54.7 Gg N) over the study period may result from transient storage in soils and aquifers, denitrification in soils, NH_3 volatilization and forest biomass storage. It should be noted that the original ReNuMa model would considerably

underestimate the riverine export fraction and aquatic denitrification fraction during 2000–2010 period, resulting in considerable overestimation of other pathways. Considering the high percentage of forests (> 65%) and large increase of N deposition over the study period (Fig. 2), ~7% of total N inputs was estimated to be retained in forest biomass in the Yongan watershed (Chen et al., 2016). Based on farmlands and animal wastes in the surrounding regions, ~16% (15–16%) of the total N input was estimated to be lost by NH_3 volatilization (Table 4). From regional soil denitrification studies (Gu et al., 2015; Wang and Yan, 2016), we estimated that 37% (33–41%) of TN inputs was removed by soil zone denitrification (Table 4). The remaining 20% (18–24%) of anthropogenic N inputs was attributed to retention in soils, vadose zone, and groundwater, highlighting the relatively strong N-leaching lag effect. This result is consistent with a modeled ~25% of total net anthropogenic nitrogen inputs retained in soils and groundwater over the past 31 years (Chen et al., 2015a) as well as a 65% increase in available N in the upper 20-cm layer of agricultural soils between 1984 and 2009 in the Yongan watershed (Chen et al., 2015b).

4.3. Implications for river N pollution control

The modified ReNuMa model provides quantitative information for N sources and loads (Fig. 6), which are essential for watershed managers making scientific decisions on N pollution controls. For example, model results will assist decision makers in making N source reductions during the best time period, such as reducing point source pollutants during the dormant season when their impact is most strongly expressed (Fig. 6c), as well as controlling nonpoint source pollution during the growing season when eutrophication is most likely (Fig. 6b). Although point sources contributed a small proportion (< 15%) compared to nonpoint sources in the Yongan watershed, the increasing point source absolute mass and contribution to the N load (Fig. 6a) suggest that domestic/industrial wastewater should be increasingly targeted to reduce TN inputs into rivers. In the short-term, managers should pay more attention to reduce surface runoff of nonpoint source N loads (Fig. 6a) by way of sink interceptions (e.g., wetlands, riparian buffers, and ecological ditches; Mander et al., 2005; Mitsch and Day, 2006), with a particular focus on the growing season. While atmospheric N deposition was high in this watershed (> 20 kg N ha^{-1} yr^{-1}, Fig. 2c), its reductions are not easily achieved by local management efforts.

The relatively long lag times (~13 years; Fig. 4a) and high groundwater contribution to riverine TN export load (mean: ~67%; 58–81%; Fig. 6a) indicated that reductions in nonpoint source N inputs may not be apparent in reduced riverine N loads for at least a decade in the Yongan watershed. Therefore, nonpoint source N pollution management decisions made on model results using short-term data sets (< 10 years) could be misleading. This provides the public with the perception that the scientific response failed to yield the expected improvements in river water quality after implementing N pollution control measures for many years (Howden et al., 2011; Bouraoui and Grizzetti, 2014). It is necessary to optimize nonpoint source N pollution control expenditures, strategies, and schedules, as well as to set appropriate expectations for the public in long-term perspective (Sanford and Pope, 2013; Bouraoui and Grizzetti, 2014). To reduce groundwater contributed TN load to rivers (Fig. 6a), measures to restore riparian zone/hyporheic zone exchange are critical for mitigating groundwater N load, including enhancing surface-groundwater hydraulic gradients, increasing hydraulic conductivity of sediments and providing sources of available carbon to riparian zone/hyporheic zone sediments (Hester and Gooseff, 2010).

5. Conclusions

This study proposed two modifications for the ReNuMa model to quantify long-term changes in riverine nitrogen sources, without adding excessive model complexity or increased data requirements. For the Yongan watershed, the modified model incorporating yearly changes in atmospheric N deposition and a N-leaching lag effect algorithm considerably enhanced model performance. A comparison of model outputs between the original ReNuMa model and the modified ReNuMa model indicated increased NS model efficiency values on the order of 0.17 to 0.24. The ability of the modified model to apportion N exports to different N sources provides decision-makers with critical information to design and implement N pollution control measures. Based on the model outputs, quantitative estimates for riverine N sources (i.e., point vs. nonpoint source, surface runoff vs. groundwater) and different N sinks (e.g., denitrification, transient storage, biomass storage) were identified to inform closure of the N budget for the Yongan watershed. This study demonstrates the importance of considering the lag effect and annual changes in atmospheric N deposition in the ReNuMa model, as well as other relevant models for simulating long-term watershed N dynamics.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhydrol.2018.03.068.

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