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A modified load apportionment model for identifying point and diffuse source nutrient inputs to rivers from stream monitoring data

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SUMMARY

Determining point (PS) and diffuse source (DS) nutrient inputs to rivers is essential for assessing and developing mitigation strategies to reduce excessive nutrient loads that induce eutrophication. However, application of watershed mechanistic models to assess nutrient inputs is limited by large data requirements and intensive model calibration efforts. Simple export coefficient models and statistical models also require extensive primary watershed attribute information and further they cannot address seasonal patterns of nutrient delivery. In practice, monitoring efforts to identify all PSs within a watershed are very difficult due to time and economic limitations. To overcome these issues, based on the fundamental hydrological differences between PS and DS pollution, a modified load apportionment model (LAM) was developed relating the river nutrient load to nutrient inputs from PS, DS and upstream inflow sources while adjusting for in-stream nutrient retention processes. Estimates of PS and DS inputs can be easily achieved through Bayesian calibration of the five model parameters from commonly available stream monitoring data. It considers in-stream nutrient retention processes, temporal changes of PS and DS inputs, and nutrient contributions from upstream inflow waters, as well as the uncertainty associated with load estimations. The efficacy of this modified LAM was demonstrated for total nitrogen (TN) source apportionment using a 6-year record of monthly water quality data for the ChangLe River in eastern China. Aimed at attaining the targeted river TN concentration (2 mg L^{-1}), required input load reductions for PS, DS and upstream inflow were estimated. This modified LAM is applicable for both district-based and catchment-based water quality management strategies with limited data requirements, providing a simple, effective and economical tool for apportioning PS and DS nutrient inputs to rivers.

1. Introduction

Excessive nutrients (e.g., nitrogen and phosphorus) in rivers is of increasing concern worldwide (Pieterse et al., 2003; Edwards and Withers, 2008; Howden et al., 2011), as it not only degrades riverine ecosystems and decreases the quality of water used for drinking, industry, agriculture, recreation, and other purposes (Bowes et al., 2010; Houser and Richardson, 2010), but also is a contributor to eutrophication and hypoxia in downstream lakes, estuaries and coastal waters (Diaz and Rosenberg, 2008; Gao and Zhang, 2010; Trevisan et al., 2012). To reduce excessive nutrient loads carried by rivers in an efficient and cost-effective manner, assessing nutrient input loads from point (PS) and diffuse sources (DSs) is required for developing watershed management and control strategies, such as the Total Maximum Daily Load (TMDL) program (Freedman et al., 2008; Bowes et al., 2009; Chen et al., 2012).

Many numerical models, ranging from simple export coefficient models (Johnes, 1996), to statistical models such as SPARROW (Smith et al., 1997), to complex mechanistic models such as AGNPS, HSPF and SWAT (Borah and Bera, 2004), have been developed for assessing watershed-scale nutrient fate and transport and nutrient source apportionment. A major limitation of these watershed mechanistic models is that they require a large amount of data for calibration for a given watershed making their application difficult for the large number of watersheds requiring assessment (Shrestha et al., 2008; Shen and Zhao, 2010; Chen et al., 2012). For example, most states in the USA lack sufficient data to quantify DS loads, with no estimates of DS loads for 20% of watersheds undergoing TMDL development (Freedman et al., 2008). Similarly, export coefficient and statistical models require considerable information on primary watershed attributes (such as land-use,

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population, agricultural census data), and knowledge of nutrient discharge from PSs (e.g., sewage treatment works and industrial discharge) (Bowes et al., 2009). Although determining nutrient loads discharged from the PSs is relatively easy in concept, it is still difficult to capture all wastewater discharge within a watershed or a district in practice due to time and economic limitations, especially in developing countries with limited PS disposal regulations. Another important consideration is that export coefficient and statistical models usually operate on an annual time step, so they cannot easily be used to infer seasonal or storm-event patterns of nutrient delivery. Such temporal 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 is most likely to occur in downstream water bodies (May et al., 2001; Bowes et al., 2008, 2009). Therefore a robust method is required for PS and DS nutrient source apportionment with high temporal resolution and limited data requirements.

Recently, the load apportionment model (LAM), which statistically quantifies the PS and DS nutrient inputs as a power-law function of the river discharge, has been proposed and successfully applied to a range of catchments of varying sizes, geologies and land uses (Bowes et al., 2008, 2009, 2010). LAM is based on the fundamental hydrological differences in the characteristics of nutrient inputs from PS and DS types. Point source nutrient input to the river is relatively constant and hydrologically independent. In contrast, DS nutrient inputs have a strong hydrologic dependence (Edwards and Withers, 2008). The LAM approach provides a simple and efficient tool for nutrient source apportionment with high temporal resolution based on routine stream monitoring data. With increasing concern for environmental water issues, many local authorities and states have carried out routine river monitoring programs (e.g., weekly, fortnightly, monthly, seasonally) to support water quality assessment and management plans (Bowes et al., 2008; Shrestha et al., 2008). These data sets, in conjunction with accompanying stream flow data, provide a fundamental data required to develop a LAM for a given watershed.

Existing LAMs still contain several important limitations. First, they assume that nutrients are relatively conservative during transport, rendering them unsuitable for rivers with high in-stream nutrient retention efficiency (Bowes et al., 2009). In-stream nutrient retention, which often accounts for an important fraction (1–80% for nitrogen and 20–70% for phosphorus) of the annual total nutrient load (Haag and Kaupenjohann, 2001; Grizzetti et al., 2005; Dierk and Michael, 2008; Chen et al., 2010), is significantly modified by river hydrological, morphological and ecological conditions (Alexander et al., 2000; Pieterse et al., 2003; Trevisan et al., 2012). Second, conventional LAMs usually assume that the PS inputs are constant throughout the year or a study period, which is generally true, but it may be not the case for some regions. For example, it is frequently observed that enterprises discharge sewage without permission or in excess of their discharge limits to maximize their profits in many regions of China (Sun and Yang, 2006; Qian et al., 2007), which could introduce a considerable error in LAM results. Third, nutrient inflows from upstream water bodies (representing the contribution from the upstream regions) are not addressed for a river-reach segment in LAM models; thus they do not satisfy requirements for district-based environmental water management. For example, in China a river is usually divided into several segments that are regulated by corresponding districts (Shang et al., 2012); thus the reach-end corresponding to the boundary between districts is commonly used as the compliance location for water quality management and regulation (Chen et al., 2009; Shang et al., 2012). Fourth, conventional LAMs often adopt a trial-and-error procedure for calibrating the model parameters, which is subjective and uncertain (Shen et al., 2006), considering the uncertainties involved in the observed data, model parameters and model structure (Howden et al., 2011; Chen et al., 2012). Uncertainty is an important issue that requires addressing in water quality model development and application (NRC, 2001). To fully exploit available monitoring data for supporting water quality management, there is an excellent opportunity to modify conventional LAMs to address these identified limitations.

This study aimed to modify conventional LAMs to make them more robust and less sensitive to the previously mentioned model limitations (e.g., in-stream nutrient retention, temporal changes in PS discharge, boundary conditions, and uncertainty involved in calibrating model parameters). The modified LAM statistically relates the river nutrient load to nutrient inputs from PS, DS and upstream inflow sources while adjusting for in-stream nutrient retention processes. Beyond the commonly used trial-and-error procedure for calibration, the Bayesian statistical method coupled with the Markov Chain Monte Carlo (MCMC) algorithm, which optimally utilizes information from both prior knowledge and observed data (Shen and Zhao, 2010; Chen et al., 2012), was adopted for calibrating the model parameters and addressing the uncertainty associated with input load estimations. The efficacy of the modified model was demonstrated through application for total nitrogen source apportionment in the ChangLe River in eastern China using a 6-year record of monthly water quality data. The modified LAM was aimed at attaining the target total nitrogen concentration (2 mg L^{-1}) and at determining the required input load reductions for PS, DS and upstream inflow nutrient loads. This modified model adopts the merits but overcomes the limitations mentioned above for conventional LAMs and statistical models. It has limited data requirements and provides researchers and managers with a simple, effective and economical tool for apportioning PS and DS nutrient inputs to rivers.

2. Materials and methods

2.1. Study area

The ChangLe River watershed (120°35′56″–120°49′03″E and 29°27′98″–29°35′12″N) is located in Zhejiang Province, eastern China (Fig. 1). The ChangLe River is one of the main tributaries of the Cao-E River, which ultimately flows into the Qiantang Estuary and East China Sea. The river system drains a total area of 864 km^2 and flows about 70.5 km with a 0.36% gradient and a 40–70 m width. The portion of the watershed examined in this study contained two sub-catchments: Sub-catchment I corresponding to the reach from S1 (NanShan Reservoir) to S2 (midstream site) and sub-catchment II corresponding to the reach from S2 to S3 (downstream boundary or watershed outlet) (Fig. 1 and Table 1). The area represents a typical agricultural watershed in eastern China and is characterized by a subtropical monsoon climate. Long-term average annual rainfall is 1256 mm with more than 65% of rainfall usually occurring between May and September. The primary land-use categories are woodland and farmland (including paddy fields, uplands, and garden plots) (Table 1). Water input from NanShan Reservoir (S1) accounts for 8 ± 5% of the annual cumulative discharge at S3 due to export for drinking water. Therefore catchment runoff from below S1 is the main water source (92 ± 7%) at the watershed outlet.

2.2. Basic data collection

Total nitrogen (TN) concentrations at three sampling sites (S1–S3) along the ChangLe River were monitored monthly from January 2004 to December 2009 (n = 72 samples per site) (Fig. 1). Water samples for chemical analysis were collected between 9 am and 2 pm in 2.5 L polyethylene bottles from 30 cm below the

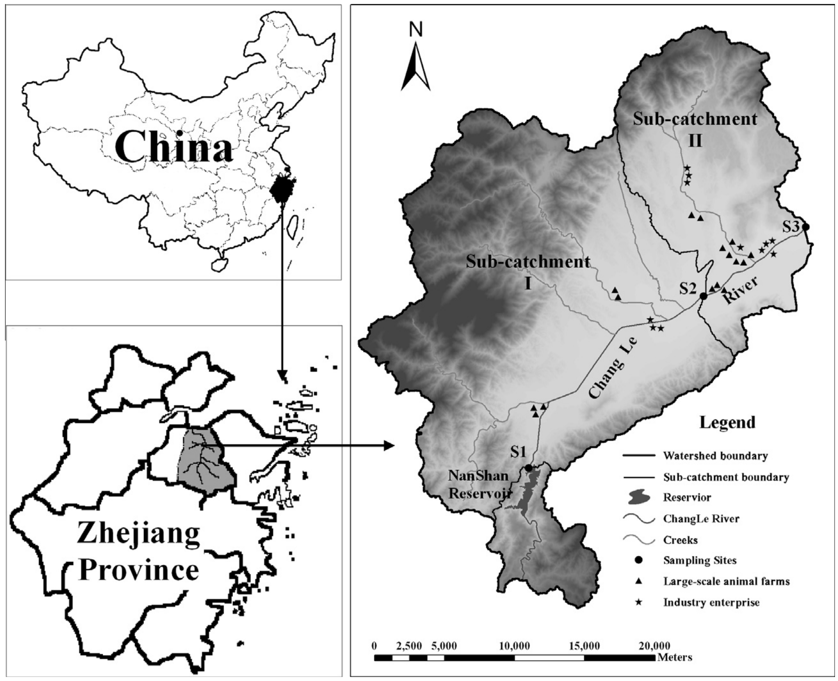

Fig. 1. Geographical location of and sampling sites at the ChangLe River watershed.

Table 1
The characteristics of the ChangLe River watershed in 2004–2009.

Sub-catchment		I	II
Catchment area (km^2)		456	195
Woodland (%)		51 ± 3	43 ± 4
Paddy field (%)		19 ± 1	24 ± 3
Upland (%)		4 ± 1	4 ± 1
Garden plot (%)		18 ± 1	16 ± 1
Residential land (%)		6 ± 1	10 ± 1
Other (%)		2 ± 1	3 ± 1
Population (person km^{-2})		331 ± 15	544 ± 26
Chemical nitrogen fertilizer application (kg N ha^{-1} yr^{-1})		134.9 ± 16.2	124.5 ± 13.3
Identified industry enterprises	Wastewater discharge ($\times 10^3$ m^3 yr^{-1})	27.8 ± 8.1	52.2 ± 9.3
	Nitrogen discharge (t N yr^{-1})	0.1 ± 0.1	0.2 ± 0.2
Large-scale animal breeding farms	Wastewater discharge ($\times 10^3$ m^3 yr^{-1})	44.4 ± 9.6	75.6 ± 11.1
	Nitrogen discharge (t N yr^{-1})	30.2 ± 4.1	50.9 ± 6.5
Household animal breeding farms	Livestock quantity (head km^{-2})	395 ± 90	831 ± 354
	Poultry quantity (head km^{-2})	285 ± 151	634 ± 369
Atmospheric deposition (kg N ha^{-1} yr^{-1})		74 ± 8	
Average daily river water discharge (m^3 s^{-1})		4.6 ± 12.1 (S2)	9.9 ± 18.3 (S3)
Average daily water temperature (°C)		19.8 ± 7.6 (S2)	19.7 ± 7.5 (S3)

water surface from three well mixed points within the cross section at each site. Water samples were acidified with H_2SO_4 in the field (15 mL concentrated H_2SO_4 per 2.5 L sample). Total N concentration was measured within eight hours of sampling using the persulfate digestion-UV spectrophotometric method. Continuous daily river discharge and water temperature at the three sampling sites were supplied by the Zhejiang Provincial Government Hydrology Office, China. According to the flow duration curve generated from the relationship between continuous daily river discharge at the watershed outlet (S3) and its corresponding exceedance percentile for the 2004–2009 study period (Chen et al., 2012), daily river discharge on the 72 field observation dates fell within the 1.1–99.5% flow exceedance interval, i.e., 29.2%, 48.6% and 22.2% of observations fell within the high (0–30th percentile), median (30–70th percentile) and low (70–100th percentile) flow regimes, respectively. Daily TN load at each sampling site for each field observation date was calculated by multiplying the TN concentration by the daily river discharge. Although there was no correlation between TN concentration and water discharge at S1 due to mixing within Nanshan Reservoir (Fig. 2), there was a significant correlation between TN load (y) and water discharge (x) at S1 ($y = 7.31x^2 + 273x - 8.16$, $R^2 = 0.91$, $n = 72$); thus daily inflow TN loads from S1 on dates not measured were predicted using daily average river water discharge from 2004 to 2009. All statistical analyses were determined using SPSS statistical software (Version 16.0; SPSS Inc. Chicago, USA).

To estimate watershed diffuse source TN input load to the river system using the export coefficient model, data on human population, livestock-poultry quantities, chemical nitrogen fertilizer application quantity, and the land-use types in the ChangLe River watershed in 2004–2009 were obtained from the Shengzhou City Agriculture Bureau of Zhejiang Province (Table 1). Annual TN input from atmospheric deposition during 2004–2009 was provided by Shengzhou City Environment Protection Bureau of Zhejiang

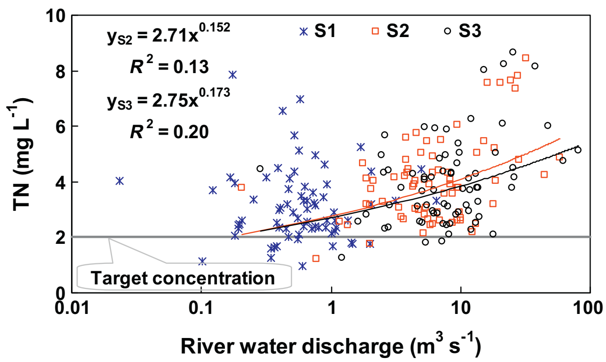

Fig. 2. Relationships between river TN concentration and water discharge in three sampling sites of the ChangLe River watershed.

Province. There is no centralized sewage collection and treatment for industrial and domestic wastewater in the ChangLe River watershed. Monitoring results from the local environmental protection bureau in 2004–2009 identified 11 industrial enterprises that have independent sewage outlets with an average annual total effluent of 80×10^3 m^3 after primary treatment (TN input load ~0.4 t yr^{-1}) and 16 large-scale animal breeding farms with an average annual total effluent of 120×10^3 m^3 without treatment (TN input load ~80 t yr^{-1}) (Table 1 and Fig. 1).

2.3. The modified load apportionment model

The modified LAM was inspired by the load apportionment concept (Bowes et al., 2008, 2009) using a statistical modeling methodology (Smith et al., 1997; Grizzetti et al., 2005). The ChangLe River watershed was subdivided into two sub-catchments/districts according to data availability. In each sub-catchment, the TN load was related to the sum of nutrient inputs from different sources and reduced by TN retention processes occurring along the river. The river nutrient load at the outlet of a sub-catchment on the ith day (L_i, kg d^{-1}) is expressed as:

$$L_i = (P_i + D_i + U_i)R_i \tag{1}$$

where P_i, D_i and U_i are nutrients input to river (reach) from PS, DS, and the upstream water bodies (kg d^{-1}), respectively. R_i is the in-stream retention factor for TN (dimensionless).

TN input loads from PS and DS are modeled as power-law functions of the daily average river discharge (Q_i, m^3 s^{-1}) (Bowes et al., 2008).

$$P_i = AQ_i^B \quad \text{and} \quad D_i = CQ_i^D \tag{2}$$

where A, B, C and D are model parameters.

Total N retention in surface waters is primarily determined by the residence time, contact area at the sediment–water interface and biological activity (Alexander et al., 2000; Haag and Kaupenjohann, 2001; Chen et al., 2010). Residence time decreases with increasing river discharge, reducing the opportunity and duration for different biogeochemical reactions to remove nutrients (Madsen et al., 2001; Smith et al., 2008). Nutrient retention capacity decreases with increasing river discharge as the contact surface between sediment and river water is also reduced (or increasing volume:surface area ratio), decreasing nutrient processing efficiency (Alexander et al., 2000; Pieterse et al., 2003; Chen et al., 2011a). Higher water temperature also increases the activities of aquatic organisms that facilitate N assimilation, such as denitrification and aquatic plant or algae uptake (Dierk and Michael, 2008; Chen et al., 2010; Houser and Richardson, 2010). Therefore, temporal variation of in-stream TN retention efficiency was related to the river discharge and water temperature in the modified LAM. The in-stream retention factor R_i was parameterized as an exponential decreasing function (Smith et al., 1997; Grizzetti et al., 2005):

$$R_i = e^{-Eq_i t_i} \tag{3}$$

where q_i and t_i are normalized river discharge (dimensionless) and water temperature (dimensionless), respectively; and E is the model parameter (dimensionless) representing in-stream retention processes. In contrast to increasing water temperature, the river discharge variable has a negative effect on in-stream nutrient retention efficiency; thus it was converted to the reciprocal form before scaling. The daily river discharge and water temperature (T_i, °C) were both reduced to the same scale by scaling as a function of the maximum value for the study period (Grizzetti et al., 2005):

$$q_i = \frac{Q_i^{-1}}{\max(Q_i^{-1})}; \quad t_i = \frac{T_i}{\max(T_i)} \qquad \text{for} \quad i = 1, \ldots, n \tag{4}$$

Therefore, river nutrient load at the outlet of a sub-catchment on the ith day is expressed as:

$$L_i = (AQ_i^B + CQ_i^D + U_i)e^{-Eq_i t_i} \tag{5}$$

As for conventional LAMs, this modified LAM (Eq. (5)) is based on the assumption that PS and DS nutrient inputs are rain/runoff-independent and rain/runoff-dependent, respectively. In Eq. (5), the parameter A represents the potential for TN load entering the river from all PSs. The changing rate of TN load input from all PSs is described by combining parameter B with river discharge. This is based on the consideration that TN input load is increased with increasing PS sewage discharge resulting in increasing river discharge although PS input is rain/runoff-independent. The parameter C describes the potential for TN loads entering the river from all DSs. The changing rate of TN load input from DSs is described by combining parameter D with river discharge. This is based on the consideration that DS TN input load is rain/runoff-dependent and increases with increasing river discharge. The parameter E describes in-stream nutrient retention potential. The changing rate of in-stream retention efficiency is described by combining parameter E with the normalized river discharge and water temperature.

The five model parameters in Eq. (5), i.e., A, B, C, D and E, are unique for a given sub-catchment under study during periods without significantly changing pollution control efforts. For cases where DS and PS discharge are changing within a watershed over time, the long-term monitoring dataset should be divided into several annual time steps to take into account changing DS and PS inputs due to mitigation efforts (Bowes et al., 2009).

2.4. The methods for calibrating model parameters

In this case study, the five model parameters for sub-catchments I and II and for the entire ChangLe River watershed were separately calibrated from 72 records for daily river TN concentration, water discharge and temperature collected monthly between 2004 and 2009. Two methods were adopted for calibrating the five model parameters, i.e., a trial-and-error procedure (TEP) using the Solver function in Microsoft EXCEL© that is commonly used in conventional LAMs and a Bayesian statistic approach using WinBUGS 1.4 software. The agreement between measured and model predictions was evaluated using correlation (R^2) and Nash–Sutcliffe coefficients (Nash–Sutcliffe coefficients >0.65 indicating a satisfactory modeling result in general, Borah and Bera, 2004).

Firstly, the five model parameters were calibrated by TEP to provide the closest fit to the observed river TN concentration and water discharge datasets. To minimize the dependence of differences in terms of magnitude between observed and predicted nitrogen loads during the study period, the error minimization algorithm was applied after both sides of Eq. (5) were converted to logarithmic form (Smith et al., 1997; Grizzetti et al., 2005). Two constraints were further imposed on the model to provide realistic solutions. First, it was assumed that $0 \leqslant B \leqslant 1$, which implies that the PS-derived TN concentration decreases with increasing river discharge (Bowes et al., 2008, 2009, 2010) and PS-derived TN load increases with increasing sewage discharge quantity, which is in favor of increasing river discharge. Second, the model was constrained to only consider $D > 1$, as DS derived TN load and concentration both increase with increasing river discharge (Bowes et al., 2008).

Secondly, a Bayesian approach coupled with the Markov Chain Monte Carlo (MCMC) algorithm was performed using WinBUGS 1.4 to calibrate model parameters, as well as to address the associated uncertainty (Chen et al., 2012). Detailed descriptions of the Bayesian approach and the code for WinBUGS software are available in Shen and Zhao (2010) and Chen et al. (2012). The prior distribution of these five target parameters was assumed to follow uniform distributions with the range of $(0, 3X)$ (Shen and Zhao, 2010). Here, X was the value of each parameter derived from the TEP method. To obtain the best-fit posterior model parameters A, B, C, D, and E, the MCMC simulation was performed using 10,000 runs until the model successfully converged (i.e., Monte Carlo errors <10% of SD). 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 for posterior simulation of nutrient source apportionment and required nutrient input load reduction to reduce autocorrelation (Shen and Zhao, 2010).

2.5. Posterior simulations of nutrient source apportionment

The river discharge at which the estimated TN inputs from PS and DS were equal (Q_e) was calculated using the coupled posterior model parameters A, B, C, and D as follows (Bowes et al., 2008):

$$Q_e = \left(\frac{A}{C}\right)^{1/(D-B)} \tag{6}$$

When river discharge is less than Q_e, PS will dominate the TN load as compared to DS. Conversely, DS will dominate the TN load compared to PS loads when river discharge is greater than Q_e.

The coupled posterior model parameters derived from the 72 field monitoring dates were applied to the daily river discharge data in 2004–2009, thereby estimating the posterior annual input of TN from PS (T_P, kg yr^{-1}) and DS (T_D, kg yr^{-1}):

$$T_P = \sum_{i=1}^{365} A Q_i^B \quad \text{and} \quad T_D = \sum_{i=1}^{365} C Q_i^D \tag{7}$$

2.6. Posterior simulations of required nutrient input load reduction

To demonstrate the application of this modified LAM for water quality management, posterior simulations of daily required TN input load reduction (RLR_i, kg d^{-1}) were performed using the coupled posterior A, B, C, D and E values. Daily maximum allowable load was estimated as the allowable total maximum daily loading that can be input to the river and still meet the required water quality target (i.e., TN = 2.0 mg N L^{-1}; Chen et al., 2012) at the sub-catchment outlet on the ith day. Then posterior RLR_i simulation was performed as:

$$RLR_i = P_i + D_i + U_i - L_{i,m} e^{E q_i t_i} \tag{8}$$

where $L_{i,m}$ is the maximum allowable river load at the outlet of a sub-catchment, which was calculated by multiplying the target TN concentration by the river discharge on the ith day.

To further apportion the posterior RLR_i among PS, DS and upstream inflow, the principle of "each polluter should answer for what he does" was adopted (USEPA, 1991). That is, the allocation of load reduction proportion for each source is directly based on its contribution proportion to the total input load.

3. Results and discussion

3.1. The model performance

The resulting parameter values (i.e., A, B, C, D and E) for the modified LAM by the trial-and-error and the Bayesian approaches are given in Table 2. The trial-and-error calibrated value of each parameter not only fell within the 95% confidence interval but also approached the mean and median values derived from the Bayesian approach. In contrast to conventional LAMs, the calibrated B parameters for the two sub-catchments and entire watershed were not equal to zero and improved the model fitting performance, indicating that PS inputs were not temporally constant (i.e., its change was reflected by changing river discharge, as PS input is mainly dependent on PS sewage discharge quantity, which further influences river discharge) over the study period. The E parameters and upstream inflow term also improved the model solution fit, indicating that in-stream retention dynamics and upstream inflow for TN should be considered. Using the calibrated model parameters from the trial-and-error procedure, observed versus modeled river TN loads and concentrations were strongly correlated with high R^2 values (>0.82) and Nash–Sutcliffe coefficients (>0.78) (Fig. 3a and b). Moreover, using the calibrated model parameters from the Bayesian approach, observed versus modeled river TN loads and concentrations were strongly correlated with more than 85% of the observed data falling within the 95% confidence interval and high R^2 values (>0.86) and Nash–Sutcliffe coefficients (>0.70) (Fig. 3c and d). These results are comparable with those for other watershed nitrogen simulations using SWAT, AGNPS and HSPF (reviewed by Borah and Bera, 2004) with Nash–Sutcliffe coefficients >0.65 for monthly simulation results for DS pollution considered good to very good.

These calibration results indicated that the modified LAM can be applied to practical water quality management, supporting the model's assumption that TN inputs from PS and DS are related to sewage discharge quantity (rain/runoff-independent) and river discharge (rain/runoff-dependent), respectively. This confirms that assumptions applied to watersheds with centralized sewage treatment facilities (Bowes et al., 2008, 2009, 2010) are also applicable for the ChangLe River watershed without centralized sewage treatment facilities. This occurs because in the absence of centralized collection and sewage treatment, TN loads derived from domestic and industrial sewage sources are directly input into the river system through numerous individual discharge channels (PS pattern). These sources are also rain/runoff-independent and follow the same assumption as PS-derived TN discharge from centralized sewage treatment facilities.

Considering the comparable calibration results obtained from two optimization methods, the model parameters derived from the Bayesian approach were used for the following load appointment and required load estimation in this study. The Bayesian approach also allows for the assessment of uncertainty, which is necessary for supporting water quality management decision making (Shen and Zhao, 2010).

Posterior annual TN input loads from DS obtained by this modified LAM were further compared to those obtained with an export coefficient model (Chen et al., 2009, 2010) and an inverse modeling approach (Chen et al., 2011a,b) for the ChangLe River watershed in previous studies (Fig. 4). Both the modified LAM and the inverse

Table 2
The modified load apportionment model parameters derived from the trial-and-error procedure and Bayesian statistical approach for TN in the ChangLe River watershed.

Sub-catchment			I	II	Entire watershed
A	Trial-and-error procedure		254	42.8	275
	Bayesian statistic	2.5%	166	18.5	194
		Mean	252	44.8	271
		Median	251	44.9	271
		97.5%	338	72.0	359
B	Trial-and-error procedure		0.264	0.323	0.274
	Bayesian statistic	2.5%	0.011	0.045	0.015
		Mean	0.263	0.617	0.332
		Median	0.229	0.675	0.303
		97.5%	0.696	0.968	0.827
C	Trial-and-error procedure		252	46.2	221
	Bayesian statistic	2.5%	152	32.0	137
		Mean	224	54.3	211
		Median	225	54.3	212
		97.5%	294	76.9	276
D	Trial-and-error procedure		1.05	1.28	1.12
	Bayesian statistic	2.5%	1.04	1.12	1.09
		Mean	1.12	1.22	1.15
		Median	1.11	1.21	1.15
		97.5%	1.20	1.33	1.22
E	Trial-and-error procedure		26.7	15.8	35.5
	Bayesian statistic	2.5%	4.4	2.9	10.9
		Mean	24.9	15.9	33.8
		Median	24.6	15.7	33.8
		97.5%	47.9	30.5	57.4

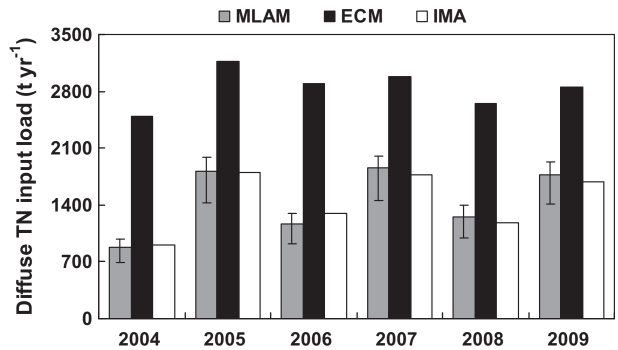

Fig. 4. Annual diffuse TN input load derived from the modified load apportionment model (MLAM) calibrated with the Bayesian approach, export coefficient model (ECM) and inverse modeling approach (IMA) in the ChangLe River watershed. The error bars indicate the 95% confidence interval for the MLAM.

modeling approach produced lower annual estimates of TN input loads compared to the export coefficient model. These disparities could be caused by the selection of inappropriate land-use or source-based TN export coefficients, as the adopted export coefficients did not consider the natural annual variability that exists for export coefficients (Bowes et al., 2008) and ignored the time delay between when nitrogen is applied to land and when the nitrogen is input to the river (Howden et al., 2011). There was close agreement in the annual TN load estimates between the modified LAM (mean values) and the inverse modeling approach (i.e., estimating catchment DS input load to rivers by the inverse format of an existing river nutrient transport equation from the river monitoring data), which further validates the efficacy of the modified LAM and supports its assumption. However, the inverse modeling approach requires more detailed information on river conditions and properties (e.g., water flow velocity, reach segment length, in-stream loss rate coefficient) (Shen et al., 2006; Chen et al., 2011a,b). Thus, the modified LAM can offer accurate estimates of the DS TN input load with minimum data requirements and less cost compared to the inverse modeling approach and export coefficient model.

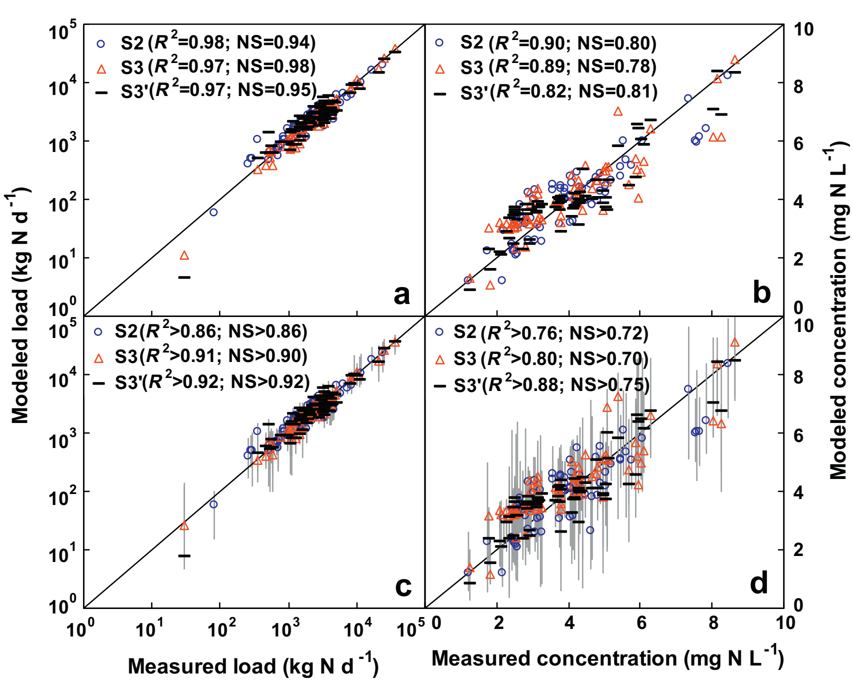

Fig. 3. The model fitting results for daily river TN load and concentration at sub-catchment I (S2), sub-catchment II (S3) and entire watershed (S3′) outlets of the ChangLe River watershed. (a) The load fitting results for the trial-and-error procedure; (b) The concentration fitting results for the trial-and-error procedure; (c) The posterior load fitting results for the Bayesian approach; (d) The posterior concentration fitting results for the Bayesian approach. The error bars indicate the 95% confidence interval. NS denotes the Nash–Sutcliffe coefficient. For the Bayesian approach, R^2 and NS were derived from observed and modeled values at posterior 2.5th percentile, mean, and 97.5th percentile.

3.2. Nitrogen source apportionment

Posterior annual TN input loads from PS, DS and upstream inflow for the ChangLe River watershed in 2004–2009 are shown in Table 3. The upstream TN inflow should be apportioned from total input load for a specific river reach catchment, as it accounted for 8 ± 1%, 67 ± 2% and 5 ± 1% of the mean annual TN input load for sub-catchment I, sub-catchment II and the entire watershed, respectively. Since the upstream inflow was considered in the modified LAM, it can be applied to multi-segment rivers for TN input load apportionment, supporting both the catchment-based and district-based (i.e., river reach) water quality management strategies.

Although the posterior mean annual PS TN input load (mean ± SD: 223.5 ± 25.2 t N yr^{-1}, Table 3) only contributed 13 ± 2% of the annual TN input load for the entire watershed, it was significantly higher than the TN input loads (mean ± SD: 84.1 ± 10.3 t N yr^{-1}) from identified industrial enterprises and large-scale animal breeding farms (Table 1). The large-scale animal breeding farms are generally located near the river (<2 km, Fig. 1) and their N-rich wastewaters are directly emitted to the river without treatment; thus these operations should be managed as PS (Yuan et al., 2011). Additionally, although sub-catchment II had larger sewage effluent and N discharge from identified PS (i.e., industrial enterprises and large-scale animal breeding farms) than sub-catchment I (Table 1 and Fig. 1), sub-catchment I had a higher PS TN input load than sub-catchment II (Table 3). This result may indicate a considerable number of unidentified PS inputs, such as illegal wastewater discharge by industrial enterprises and animal and domestic wastewater emissions from residential areas. It is frequently observed that enterprises discharge pollutants without permission or beyond pollution limits to maximize their profits and these kinds of activity mainly occur during high-flow periods in an attempt to avoid detection (Sun and Yang, 2006; Qian et al., 2007). Since there is no centralized sewage collection and treatment for domestic wastewater in the ChangLe River watershed, domestic wastewaters are often directly discharge to the river without treatment. Additionally, many household septic tanks in rural and small town areas are directly connected to the river or drainage systems, and actually operate as numerous small PS sewage inputs (Arnscheidt et al., 2007). The higher population living in sub-catchment I is consistent with higher sewage wastewater inputs contributing to PS inputs in this sub-catchment (Table 1). Due to time and economic limits, only very slow progress is being made to fully capture these widely distributed and numerous PS along the river system. The modified LAM is thus a potentially powerful tool for identifying illegal and unmonitored nutrient discharge resulting in considerable savings in monitoring costs.

Posterior mean annual DS TN input load accounted for 82 ± 3% of annual TN input load for the entire watershed (Table 3), which is consistent with previous estimates for the ChangLe River watershed (Chen et al., 2009, 2010, 2011a,b); thus river TN concentrations at sampling sites S2 and S3 were synchronously increased with increasing river discharge (Fig. 2). According to field investigations, nitrogen fertilizer application, rural domestic wastes, household livestock-poultry breeding and atmospheric deposition are the primary sources of DS TN inputs to the ChangLe River (Table 1). Although sub-catchment I produced a larger DS TN input load than sub-catchment II (Table 3), sub-catchment II had a larger area-specific DS TN input rate (mean ± SD: 24.5 ± 7.5 kg ha^{-1} yr^{-1}) than sub-catchment I (mean ± SD: 21.4 ± 5.8 kg ha^{-1} yr^{-1}) ($P < 0.01$). This is primarily related to the higher population and animal densities along with lower woodland percent in sub-catchment II than those in sub-catchment I (Table 1).

As indicated by Eq. (2) and the calibrated model parameters in Table 2, posterior daily mean TN input loads from PS (133–4692 kg d^{-1}) and DS (8.2–251,603 kg d^{-1}) synchronously increased with increasing river discharge; thus the major TN inputs are expected to occur during high river flows. The river discharge at which the PS and DS TN inputs to the river are equal (Q_e) was

Table 3
Posterior annual input load, in-stream retention load, maximum allowable input load, and required input load reduction for TN in the ChangLe River watershed (t yr^{-1}).

Sub-catchment			I	II	Entire watershed
Input load	Point source	2.5%	80.1 ± 4.1	13.9 ± 0.9	92.9 ± 4.6
		Mean	155 ± 14.2	91.2 ± 17.2	224 ± 25.2
		Median	138 ± 10.1	78.9 ± 13.4	182 ± 15.9
		97.5%	335 ± 55.5	237 ± 53.9	573 ± 107
	Diffuse source	2.5%	796 ± 218	343 ± 104	1152 ± 323
		Mean	965 ± 260	469 ± 142	1455 ± 408
		Median	975 ± 263	479 ± 147	1479 ± 417
		97.5%	1061 ± 274	556 ± 166	1602 ± 433
	Upstream inflow		93.8 ± 22.2	1062 ± 254	93.8 ± 22.2
In-stream TN retention load		2.5%	10.8 ± 0.6	15.9 ± 0.5	47.7 ± 1.8
		Mean	81.1 ± 2.6	77.7 ± 2.8	153 ± 5.6
		Median	79.9 ± 2.5	76.7 ± 2.7	153 ± 5.5
		97.5%	159 ± 4.9	144 ± 5.8	258 ± 10.8
Maximum allowable input load		2.5%	485 ± 104	216 ± 46.9	712 ± 154
		Mean	524 ± 125	247 ± 62.0	820 ± 212
		Median	519 ± 126	244 ± 59.8	823 ± 266
		97.5%	614 ± 137	323 ± 140	1003 ± 191
Required input load reduction	Point source	2.5%	38.5 ± 12.4	11.0 ± 0.6	31.7 ± 12.3
		Mean	80.8 ± 7.8	77.1 ± 14.3	105 ± 19.9
		Median	73.2 ± 5.0	66.4 ± 11.1	85.1 ± 13.5
		97.5%	180 ± 29.4	199 ± 43.8	278 ± 81.7
	Diffuse source	2.5%	466 ± 132	292 ± 80.2	570 ± 210
		Mean	561 ± 157	405 ± 124	824 ± 245
		Median	563 ± 158	414 ± 128	842 ± 253
		97.5%	623 ± 164	481 ± 145	933 ± 268
	Upstream inflow	2.5%	54.5 ± 13.1	973 ± 203	41.2 ± 20.3
		Mean	57.7 ± 14.3	1015 ± 239	56.4 ± 14.3
		Median	57.8 ± 14.3	1019 ± 242	55.1 ± 14.1
		97.5%	60.2 ± 14.6	1036 ± 247	59.4 ± 14.8

calculated by Eq. (6). The estimated mean Q_e was 1.23, 0.94 and 1.53 $m^3 s^{-1}$ for sub-catchment I, sub-catchment II and the entire watershed, respectively. This indicates that the average percentage of time that DS dominate was 98%, 99% and 98% for sub-catchment I, sub-catchment II and the entire watershed during 6-year study period, respectively. Therefore, DS should be preferentially targeted for river TN pollution mitigation in the ChangLe River watershed.

3.3. In-stream nitrogen retention efficiency

For the ChangLe River watershed, posterior mean annual in-stream TN retention load was 153.2 ± 5.6 t yr^{-1} (mean ± SD), accounting for 11 ± 4% of total input TN load in 2004–2009. This retained load was comparable in magnitude to the PS TN input load (Table 3); thus in-stream processes should be considered in river TN source apportionment. In-stream TN retention efficiency presented remarkable spatial and temporal variation resulting from varying river discharge and water temperature (Fig. 5). Sub-catchment I with lower river discharge (Table 1) had a higher posterior in-stream TN retention percentage relative to total input load (mean ± SD: 11 ± 10%) than sub-catchment II (mean ± SD: 8 ± 8%) (Fig. 5a). Over the 6-year study, posterior retention percentage decreased with increasing river discharge ($R^2 > 0.76$, $P < 0.01$), but increased with increasing water temperature ($R^2 > 0.12$, $P < 0.01$). Thus, in-stream retention efficiency will be disproportionately decreased with increasing TN input due to increasing river discharge (Peterson et al., 2003). These observed relationships between in-stream retention percentage and river discharge and water temperature are consistent with the current understanding of the biogeochemical processes responsible for in-stream TN retention (Smith et al., 1997; Alexander et al., 2000; Peterson et al., 2003; Dierk and Michael, 2008; Chen et al., 2011a). During the PS pollution dominated period or low flow period ($<Q_e$), mean in-stream TN retention percentage was >65% for each sub-catchment, partially explaining the lower TN concentrations in the low flow period (Fig. 2), in spite of less dilution capacity during this period. Due to the higher water temperature, summer (i.e., May to September) generally presented higher in-stream TN retention percentages (mean ± SD: 17 ± 13%) than the period from October to April (mean ± SD: 14 ± 11%) (Fig. 5b), which favors mitigating the larger TN input loads during the summer (Chen et al., 2010). Consequently, underestimating the percentage of TN input load due to neglecting in-stream TN retention processes will have a greater effect for sub-catchments and time periods having lower river discharge and higher water temperature.

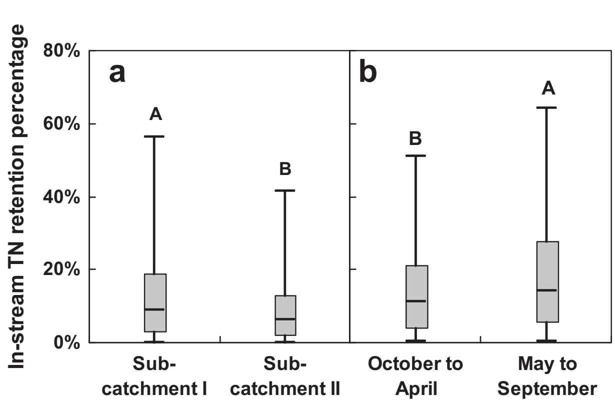

Fig. 5. Variations of posterior in-stream TN retention percentage between two sub-catchments (a) and between two periods (b) for the ChangLe River watershed. Box plots display 2.5th, 25th, 50th, 75th and 97.5th percentiles. Capital letters denote significant differences ($P < 0.01$) between two sub-catchments or two periods.

3.4. Using the modified LAM for targeting nitrogen input load reduction

The main focus of water quality management is to control pollutant loading into water bodies to ensure that water quality meets the targeted goals (NRC, 2001; Chen et al., 2009). When compared with the existing river TN concentrations for the 6-year study period, the ChangLe River failed to meet the target water quality standard for TN concentration of 2.0 mg L^{-1} (Fig. 2); thus the existing TN input loads must be appreciably reduced to attain the target in-stream TN level. Posterior mean annual required input load reduction should account for 57 ± 1%, 85 ± 1% and 54 ± 7% of the annual TN input load for sub-catchment I, sub-catchment II and the entire watershed, respectively (Table 3). Diffuse source TN inputs must be a primary target for load reduction in both sub-catchment I and the entire watershed. However, sub-catchment II requires a large reduction in the upstream TN inflow load (Table 3). Thus, attaining the target in-stream TN level for sub-catchment II is mainly dependent on achievement of the required TN input load reduction in sub-catchment I. In China, the administrative district (such as town, county or province) is the main decision-making body for regional water quality and quantity management (Shang et al., 2012). A river is usually divided into several reach segments and they are regulated by corresponding districts. The allocated input load reduction for each sub-catchment or upstream inflow in this study is equivalent to apportioning the pollution control responsibilities among districts, supporting the district-based water quality management approach.

Due to the high temporal dependence of nutrient inputs, environmental managers are often required to preferentially focus on nutrient load reduction during the sensitive summer period of enhanced algae growth (Bowes et al., 2008). Previous studies have demonstrated that lakes and estuaries in eastern China tend to have the highest risk for eutrophication during the summer (i.e., May to September) when high rainfall generates high nutrient inputs and high temperatures and sunlight stimulate algae growth (Xiao et al., 2007; Gao and Zhang, 2010). Therefore, the posterior daily required input load reduction to meet the TN water quality target for the entire watershed during the May to September period was extracted from the 6-year data record (Fig. 6). Daily required TN input load reductions for PS, DS, and upstream inflow synchronously increased with increasing river discharge ($r > 0.98^{**}$ for mean values). This indicates that generation of TN input loads was larger than the corresponding total maximum allowable load with increasing river discharge. Thus, a temporally variable expression (e.g., a function of river discharge) is required for determining input load reduction allocations (Chen et al., 2011b, 2012). The percentage of time that DS inputs dominate ($> Q_e$, Fig. 6) the required TN input load reduction was 99%, indicating the necessity for targeting DS TN reduction to attenuate the eutrophication risk for downstream waters in summer.

3.5. The model limits and implications

This modified LAM, similar to conventional LAMs, primarily relies on the quantity and quality of the data for nutrient concentrations, water discharge and water temperature. Thus, it is vital that the sampling interval is sufficiently short to capture a representative range of hydrological events for a given river system. A monthly monitoring interval, which is typical of Chinese environmental protection agencies and other government agencies, may not adequately characterize the high-flow events due to their limited occurrence throughout a given year (Johnes (2007)). The under-representation of high-flow events is also a problem for the more complex mechanistic models such as AGNPS, HSPF and SWAT (Borah and Bera, 2004). Due to the positive exponential

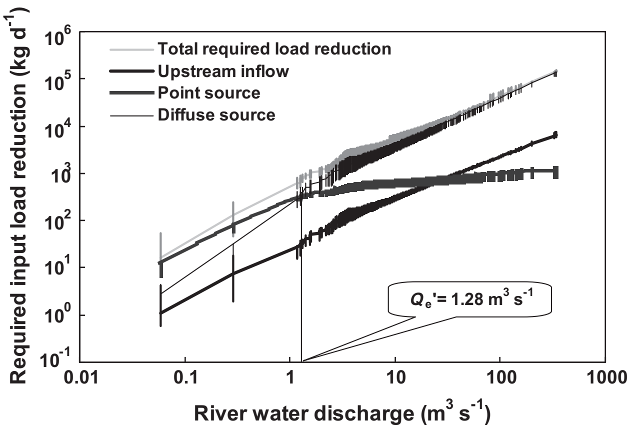

Fig. 6. Relationship between posterior daily mean required input TN load reduction for point and diffuse source inputs and river water discharge during summer (from 1st May to 30th September) in the ChangLe River watershed. $Q_{e'}$ denotes the river water discharge at which total input from the point source and upstream inflow is equal to the diffuse input to the river. The error bars i.

relationship that existed between river TN concentrations and water discharge in this DS-pollution dominated watershed (Fig. 2), under-representation of high flow events would result in an underestimation of DS TN inputs using the LAM approach. However, long-term river monitoring datasets (>5 years) are generally able to capture the full range of hydrologic conditions for a river system (Bowes et al., 2009). The observed river flows in this study fell within the 1.1–99.5% exceedance interval for daily river flows measured during the 2004–2009 study period, indicating that the monthly sampling interval was adequate for capturing high-flow events. Once the model has produced a reasonable fit to the long-term monitoring record, the empirically-fitted model parameters can be applied to high temporal-resolution river discharge data, which is generally available for most major rivers. However, a limitation of the modified LAM (as well as conventional LAMs) is that it cannot directly identify the individual contribution of specific nutrient sources (e.g., sewage treatment discharge, fertilizer application, animal and domestic wastes, etc.).

Conventional LAMs and this modified format both assume that the DS nutrient input is dependent on water flow or catchment runoff. Beyond hydrological conditions, DS nutrient input to rivers is also influenced by the crop planting and harvest dates, fertilization timing, tillage practices and land-use types (Pieterse et al., 2003; Shrestha et al., 2008; Neal et al., 2008; Howden et al., 2011). All these factors vary with time to alter temporal nutrient delivery to rivers. Although the assumption of water flow dependence for DS inputs is generally true, it may not be the case for all rivers characterized by different conditions and practices.

In contrast to conventional LAMs, this modified LAM follows the assumption that PS nutrient input load is not always temporally constant (i.e., model parameter *B* has not been assumed to be zero) and its change is reflected by changing river discharge, since wastewater discharged from all PS influences river discharge. Although this is generally true, it may not be the case for all PS input types due to changing nutrient concentration in the effluent. With increasing demands for improved water quality by the public and government, the number of sewage treatment facilities and increased nutrient removal efficiency for existing sewage treatment facilities and agricultural best management practices will increase in many regions (Neal et al., 2008). In cases where DS and PS discharges are changing within a watershed over time, the long-term monitoring dataset should be divided into several annual time steps to take into account changing DS and PS inputs due to mitigation efforts (Bowes et al., 2009). Then the success (or failure) of DS and PS pollution control efforts can be tracked by the changes in the calibrated model parameters *A*, *B* and *C*, *D*, respectively (Bowes et al., 2010).

This modified LAM considers in-stream retention processes and assumes that in-stream nutrient retention efficiency is mainly dependent on hydrological and water temperature conditions. While this is generally true, it may not be the case for all rivers, since temporal variation of in-stream nutrient retention efficiency is also subject to influence by other factors, such as the sunlight that influences aquatic plant and algae dynamics, nature and organization of the river bed, and river and sediment oxygen levels (Chen et al., 2010; Houser and Richardson, 2010; Trevisan et al., 2012). The nutrient input location for different sources affects the in-stream residence time, which also influences in-stream nutrient retention efficiency (Smith et al., 2008; Chen et al., 2011a). It should be pointed out that river nutrient concentration tends to vary diurnally due to diurnal changes of in-stream processes and catchment TN inputs (Pellerin et al., 2009; Volkmar et al., 2011). The model deals with these perturbations by adopting daily average river discharge and temperature, but may not be applicable to rivers with a high dependence of other factors for in-stream processing or rivers with large diurnal variability.

In contrast to conventional LAMs, this modified LAM calibrates the model parameters with Bayesian statistics. The resulting posterior model parameters can provide both point (such as mean and median values) and interval estimations (such as 95% confidence interval) of PS and DS input loads, in-stream retention capacity, and required load reduction (Table 3 and Figs. 5 and 6). This not only quantitatively describes the uncertainty for model estimates, but also provides a confidence level that can be easily understood by decision makers from a management point of view. If large uncertainty is associated with estimation, as indicated by a large 95% confidence interval (Chen et al., 2012), caution should be exercised and more observational data may be needed to lower the uncertainty (Shen et al., 2006; Shen and Zhao, 2010). The resulting posterior required load reductions under different confidence levels (Table 2) provide decision makers and stakeholders with an explicit basis for designing load reduction strategies, supporting the practical adaptive implementation of TMDL programs while considering uncertainty factors (Freedman et al., 2008). For example, if being conservative is a major concern for water pollution control, the upper 90% or 95% credible level of the required load reduction can be selected in practice.

4. Conclusion

Compared with conventional LAMs, the modified LAM format developed in this study considers both in-stream retention processes and changes of PS inputs during a study period, and also can address the uncertainty associated with nutrient source apportionment. In addition, it incorporates an upstream nutrient inflow term that allows application to both district-based and catchment-based water quality management strategies. Compared with other types of models, this modified LAM is much easier to apply and can produce more realistic estimates of PS and DS nutrient inputs. Since the model relates the stream nitrogen load to catchment input load, it is further capable of determining required input load reductions for PS, DS and upstream inflow sources to attain the target river nutrient level while considering uncertainty. All these model applications are easily achieved through Bayesian calibration of the five model parameters from monitoring datasets of river nutrient concentration, water discharge and temperature, which are commonly and increasingly available in many countries and regions.

For the ChangLe River watershed, estimated mean TN inputs from DS, PS and upstream inflow waters contributed 82 ± 3%, 13 ± 2% and 5 ± 1%, respectively, of the annual TN input load in 2004–2009. Mean DS inputs were greater than PS inputs 99% of the time during the 6-year study. In-stream retention processes, which accounted for 11 ± 4% of the mean annual TN input load, had a higher efficiency for sub-catchments and time periods with lower river discharge and higher water temperature. To attain the targeted water quality objective for TN concentration ($2.0\ mg\ L^{-1}$), 54 ± 7% of the mean annual TN input load needs to be reduced. Based on our analysis, TN load reduction strategies should be preferentially aimed at reductions in DS TN inputs, especially during summer high-flow periods when eutrophication risk is greatest for downstream water bodies. This case study demonstrates that the modified LAM has limited data requirements and provides researchers and managers with a simple, effective and economical tool for apportioning PS and DS nutrient inputs to rivers, as well as associated uncertainty assessment.

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