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Journal

The Science of The Total Environment, 533

ISSN

0048-9697

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Publication Date

2015-11-01

DOI

10.1016/j.scitotenv.2015.06.079

Peer reviewed

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Science of the Total Environment 533 (2015) 196–204

Contents lists available at ScienceDirect

Science of the Total Environment

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

Reconstructing historical changes in phosphorus inputs to rivers from point and nonpoint sources in a rapidly developing watershed in eastern China, 1980–2010

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HIGHLIGHTS

- Long-term TP input loads from nonpoint and point sources were determined by the LAM.
- The LAM produced river total TP loads were verified by the outputs from the LOADEST.
- In-stream retention/remobilization component of point source P load was estimated.
- Both nonpoint and point source TP input loads increased rapidly over the past 31-yr.
- Nonpoint source input dominated TP load, especially for the summer high-flow period.

ARTICLE INFO

Article history:
Received 14 April 2015
Received in revised form 26 May 2015
Accepted 20 June 2015
Available online 8 July 2015

Editor: Eddy Y. Zeng

Keywords:
Eutrophication
Agriculture
Sewage
Nutrient
Point source
Diffuse (nonpoint) source
Load apportionment model

ABSTRACT

Quantifying point (PS) and nonpoint source (NPS) phosphorus inputs to rivers is critical for developing effective watershed remediation strategies. This study reconstructed PS and NPS total phosphorus (TP) inputs to the Yongan River in eastern China in 1980–2010 using a load apportionment model (LAM) from paired riverine TP concentrations and river discharge records. Based on the fundamental hydrological differences between PS and NPS pollution, the LAM statistically quantified their individual inputs as a power-law function of river discharge. The LAM-estimated monthly/annual riverine TP loads were in good agreement with results derived from a regression model, Load Estimator (LOADEST). The annual TP load increased from 18.4 to 357.0 Mg yr^{-1} between 1980 and 2010. The PS input contributed 7–45% of annual total TP load and increased 23-fold, consistent with a 20-fold increase in flow-adjusted average chloride concentration during the low flow regime (a proxy for wastewater inputs), as well as measured increases in population, poultry, and industrial production. Inferring from observed TP and chloride ratios, as well as total suspended solids (TSS) and river discharge dynamics, temporally retained P load within the river during the low flow regime was estimated to contribute 18–65% of the annual PS input load. NPS inputs consistently dominated the annual riverine TP load (55–93%) and increased 19-fold, consistent with the strong correlation between riverine TP and TSS concentrations, increasing developed land area, improved agricultural drainage systems, and phosphorus accumulation in agricultural soils. Based on our analysis, TP pollution control strategies should be preferentially directed at reductions in NPS loads, especially during summer high-flow periods when the greatest eutrophication risk occurs.

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1. Introduction

Enrichment of phosphorus (P) is a major cause of waterbody eutrophication and associated impairments to water quality and aquatic ecosystems (Bowes et al., 2014; Sharpley et al., 2015). To reduce the negative impacts of excess P, watershed managers develop strategies to attain a target P level that can satisfy the designated use of a water body through control of anthropogenic sources (Freedman et al., 2008; Chen et al., 2012; Bowes et al., 2015). Setting P source reduction targets and identifying remedial options rely on appropriate and accurate apportionment of P loads to point (PS) and nonpoint sources (NPS) (Bowes et al., 2009a; Jarvie et al., 2012; Chen et al., 2013).

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http://dx.doi.org/10.1016/j.scitotenv.2015.06.079
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Many numerical models, ranging from simple export coefficient models, to statistical models such as SPARROW, to complex mechanistic models such as AGNPS, HSPF and SWAT (Moriasi et al., 2007; Shrestha et al., 2008; Chen et al., 2013), to Material Flow Analysis (Schaffner et al., 2009), are available for assessing watershed-scale nutrient source apportionment. A major limitation of these watershed mechanistic models as well as Material Flow Analysis method is that they require a large amount of detailed data for calibration of a given watershed making their application challenging for the large number of watersheds requiring assessment (Freedman et al., 2008; Shrestha et al., 2008; Chen et al., 2013). Lumped models, which usually provide a simplified understanding of nutrient sources and transfer dynamics from the watershed to rivers, also require information on primary watershed attributes (e.g., land use, population, and agricultural census data), as well as nutrient discharge from sewage treatment facilities and industries. However, accurate datasets spanning a number of decades are relatively rare for most watersheds, especially in developing countries experiencing the most severe nutrient pollution (Freedman et al., 2008; Bowes et al., 2009a). The source apportionment results determined from current models are also subject to considerable uncertainty since measured riverine P loads are a mixture of P-rich waters having different ages (Sharpley et al., 2013; Jarvie et al., 2013). Very often the lag time (ranging from several years to decades) between legacy P inputs and riverine export is much larger than the temporal extent of available watershed attributes and river monitoring data (Meals et al., 2010; Kleinman et al., 2011). Therefore, these models still encounter several challenges for determining long-term changes in PS and NPS contributions.

Based on the fundamental hydrological differences between nutrient inputs from PS and NPS to rivers, a load apportionment model (LAM) may be developed for statistically quantifying point and nonpoint source nutrient inputs as a power-law function of river discharge (Bowes et al., 2008, 2009a, 2009b, 2010, 2014; Greene et al., 2011; Chen et al., 2013). The LAM does not require detailed watershed attribute information and can potentially be applied to any dataset comprised of paired P concentrations and river discharge measurements. This approach has been successfully applied to a wide range of watersheds in England, Ireland, U.S.A. and China (Bowes et al., 2008, 2009a, 2009b, 2010, 2014; Greene et al., 2011; Jarvie et al., 2012; Chen et al., 2013). In terms of long-term riverine P source apportionment, however, existing LAM applications encounter some important limitations. First, point source P inputs can be temporally retained within the river network via a range of abiotic and biotic processes (e.g., sorption to stream sediments, periphyton uptake) during the low flow regime, with the retained P being subsequently remobilized via erosion of fine bed sediments, advective release of dissolved P from pore waters, or scouring of biologically incorporated P from benthic sources during storm events (Schaffner et al., 2009; Bowes et al., 2010, 2015; Jarvie et al., 2012, 2013; Sharpley et al., 2013; Hayakawa et al., 2015). In conventional applications of LAMs, the remobilization of P from the river channel is incorrectly assigned to the nonpoint source input load, which leads to overestimation of P from NPS and underestimation of PS. A second limitation for conventional LAM application is that they are usually validated from the results of other models, commonly export coefficient models (Bowes et al., 2008, 2009a, 2009b, 2010). However, it remains a challenge to verify LAM results using export coefficient based models for many watersheds since long-term specific P export coefficients are not available or rapidly changing over time. Due to time and economic constraints, it is difficult to capture all wastewater discharges within a watershed, especially in developing countries where limited wastewater collection and treatment is practiced (Chen et al., 2013). This results in difficulty for verifying LAM point source load estimates by direct comparison to wastewater discharge records.

Since the 1980s, many Chinese rivers have experienced a significant increase in nutrient concentrations and loads associated with intensive crop cultivation, livestock production, human population expansion, and urbanization (Liu et al., 2003; Li et al., 2007; Yu et al., 2010). Although eastern China has experienced the most rapid economic development since the 1980s, little information concerning long-term changes in the distribution of PS and NPS nutrient pollution is available for rivers in eastern China. Coastal waters along the East China Sea, as well as many inland lakes and reservoirs, have excessive nutrient inflows from upstream rivers resulting in increased hypoxia/anoxia and risks to drinking water safety from harmful algal blooms (Yang et al., 2013; Huang et al., 2014). Accordingly, it is urgent to establish quantitative knowledge for PS and NPS P inputs to rivers in eastern China over the past several decades to guide effective control strategies for rapidly increasing P pollution.

Using the LAM approach, this study reconstructs the historical (1980–2010) changes in PS and NPS total phosphorus (TP) loads in the Yongan River watershed in eastern China. To deal with the challenges and limitations for conventional LAM applications, this study: (1) addresses the instream retention/remobilization P load from PS during the low flow regime based on the TP:chloride ratio to calibrate the LAM apportioned PS and NPS P inputs; and (2) employs a regression model, Load Estimator (LOADEST, Runkel et al., 2004), that can estimate long-term change in riverine nutrient loads as functions of water discharge and time to verify the LAM results. To conform to the LAM assumption that changes in PS and NPS pollution are primarily regulated by hydrological conditions, the 31-yr record was statistically divided into 5 time periods according to changing trends in flow-adjusted TP and chloride concentrations for separate calibration the LAM. Novel aspects of this study include improvements of the LAM to provide more accurate apportionment of riverine P loads and reconstructing the first historical quantification of PS and NPS pollution for a typical river in eastern China. The results of this study advance our quantitative knowledge of long-term riverine P pollution dynamics and inform P management strategies to effectively assess and control pollution at the watershed scale.

2. Materials and methods

2.1. Watershed description

The Yongan River watershed (120° 13′ 46.065″–121° 0′ 52.464″E and 28° 28′ 10.118″–29° 2′ 22.156″N; elevation ~15–1000 m) is located in the highly developed Taizhou City area of Zhejiang Province, China (Fig. 1). The Yongan River is the third largest river of Zhejiang Province and flows through Xianju County and Linhai City to the Taizhou Estuary and the East China Sea. The sampling location (Fig. 1) for this study was 55 km upstream of Taizhou Estuary at an elevation of ~15 m. The river drains a total area of 2474 km^2 and has an average annual water depth of 5.42 m and discharge of 72.9 $m^3\ s^{-1}$ (mean summer vs winter discharge = 122 vs 30 $m^3\ s^{-1}$) at the sampling location. The climate is subtropical monsoon having an average annual temperature of 17.4 °C and average annual precipitation of 1400 mm (Supplementary material: Fig. S1a). The rainfall mainly occurs in May–October with a typhoon season occurring in July–September. Total population within the watershed increased from ~590,000 in 1980 to ~740,000 in 2010 (Supplementary material: Fig. S1b), with ~67% in the Xianju County and 33% in the Linhai City. Over the 31-year study period, domestic livestock production (pig, cow, sheep and rabbit) decreased by ~25% while poultry production (chicken and duck) increased by 4.8-fold. Agricultural land (including paddy field, garden plot and dryland) averaged ~12% of total watershed area in 1980–2010, with developed land (including rural and urban residential lands, roads, and mining and industry lands) and natural land (woodland, water surface, swamp, rock, and natural reservation land) contributing ~3% and ~85%, respectively (Supplementary material: Fig. S1c). The economic role of agriculture has been increasingly replaced by industry (with a 200-fold increase in industrial gross domestic production, Fig. S1b), resulting in a remarkable reduction (~37%) in chemical P fertilizer application since 2000. The agricultural land area with

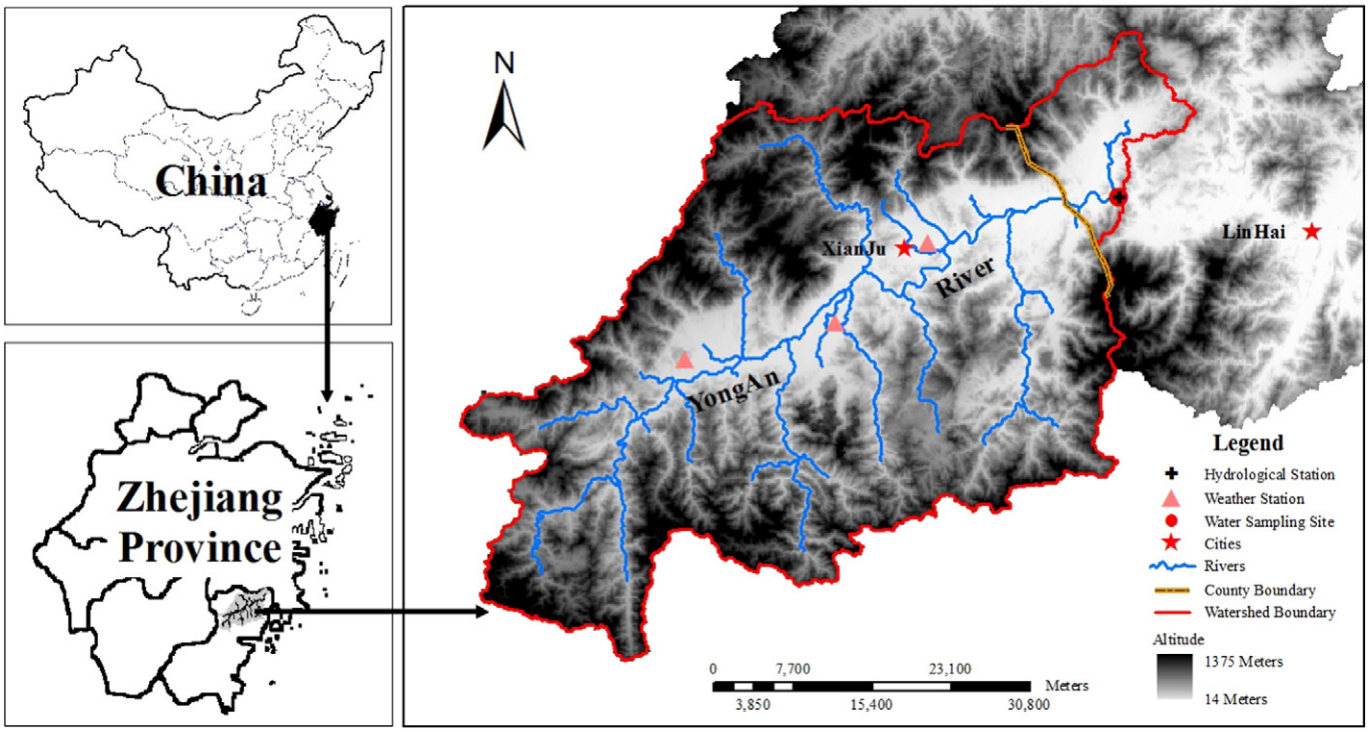


Fig. 1. Location of the Yongan River watershed in Zhejiang Province and its water quality, weather and hydrology monitoring stations.

efficient drainage systems (e.g., cement channels and pipes) increased by ~86% (Supplementary material: Fig. S1c).

2.2. Data sources

River water samples were collected once every 4–8 weeks at Baizhiao station from 1980 to 2010 (Fig. 1) by the local environment protection bureau. A well-mixed composite water sample (surface and bottom layers at three sites along the cross section) was collected between 8:00 and 9:00. Duplicate samples from the composite sample were analyzed within 4 h of collection. TP (dissolved + particle phosphorus), chloride (Cl^-), and total suspended solids (TSS) concentrations were determined by the spectrophotometric ammonium molybdate, silver nitrate titration, and gravimetric methods, respectively (Yu et al., 2010; Chen et al., 2015). Daily river discharge at Baizhiao station (Fig. 1) and daily precipitation at three weather monitoring stations within the watershed were obtained from the local hydrology and weather bureaus, respectively. The high flow regime (0–10% exceedance percentile) was determined by the river discharge duration curve method (Chen et al., 2012). Population, domestic animal, and land-use statistics for 1980 to 2010 were derived from the annual Statistic Yearbook for Xianju County and Linhai City (Chen et al., 2015).

2.3. The load apportionment model

Due to the fundamental hydrological differences between nutrient inputs from point (PS) and nonpoint sources (NPS), riverine TP load on the *i*th day (L_i, kg P d^{-1}) can be expressed as (Bowes et al., 2008, 2009a, 2009b):

$$L_i = AQ_i^B + CQ_i^D \quad (1)$$

where *A*, *B*, *C* and *D* are model parameters and Q_i is the daily-average river discharge ($m^3\ s^{-1}$). The *A* parameter represents the potential for TP load entering the river from all PS. Changes in TP load input from all PS are described by combining parameter *B* with river discharge. This is based on the consideration that PS contribution to TP load increases with increasing sewage discharge, resulting in increasing river water discharge (especially for the low flow regime) (Chen et al., 2013). Furthermore, the deposited (i.e., instream retention) PS P load decreases with increasing river discharge (Jarvie et al., 2012). Parameter *C* describes the potential for TP loads entering the river from NPS. The change in TP load input from NPS is described by combining parameter *D* with river discharge. This is based on the consideration that NPS TP input load is rain/river flow-dependent and increases with increasing river discharge.

The four model parameters (*A*, *B*, *C* and *D*) in Eq. (1) are unique for a given watershed during time periods when human activities remain relatively constant (i.e., changes in PS and NPS TP inputs are primarily determined by changing hydrological conditions). When significant changes in human activities occur over time, a long-term monitoring dataset should be divided into several multi-year time intervals for separately calibrating the LAM (Bowes et al., 2009a; Chen et al., 2013). Due to the difficulty in acquiring accurate long-term information on wastewater discharge for the large watershed in this study, the 31-yr time series was divided into several time intervals according to changes in the annual average flow-adjusted TP concentration (representing a net influence of human activities on PS and NPS pollution, Basu et al., 2010) and average flow-adjusted Cl^- concentrations during the low flow regime (a proxy for the net influence of human activities on PS pollution, Jarvie et al., 2012; Ding et al., 2014). Due to the absence of a significant correlation between flow-adjusted concentrations and year number ($p < 0.05$) for a time interval, watershed human activities were assumed to have no significant influence on NPS and PS pollution dynamics within a given time period. A linear regression analysis was adopted to determine the dependence of changes in annual flow-adjusted average TP and Cl^- concentrations during the low flow regime versus year number (e.g., 1, 2, 3,…10) over selected annual time steps (Chen et al., 2014). Annual flow-adjusted average concentration (C_{FN}, Basu et al., 2010) was estimated as $C_{FN} = \sum(C \times Q) / Q_a$, where C is the measured concentration for a given monitoring date, Q is the corresponding river discharge

for a given monitoring date, and Q_a is average river discharge for all monitoring dates from 1980 to 2010. Regression and correlation analyses were performed using SPSS statistical software (version 16.0, SPSS Inc., Chicago, IL, USA).

The four fitting parameters in the LAM were calibrated by least squares fit using Matlab software (version 10.0, The MathWorks Inc., Natick, MA, USA). Two constraints were imposed on the model to provide realistic solutions. First, it was assumed that $0 \le B \le 1$, which implies that the PS-derived TP load will increase and concentration decreases with increasing river discharge (Chen et al., 2013). Second, the model was constrained to only consider $D > 1$, as NPS-derived TP load and concentration both increase with increasing river discharge (Bowes et al., 2008). Furthermore, parameters A and B were both constrained as >0. The overall, as well as specific, fit between measured and modeled daily TP concentrations or loads during the monitoring dates was evaluated using correlation (R^2) and Nash–Sutcliffe coefficient metrics (Moriasi et al., 2007).

2.4. The LOADEST model

To verify the LAM results, the widely applied Load Estimator (LOADEST) model was used to predict monthly and annual riverine TP load in the Yongan River for 1980–2010. LOADEST uses time-series river water discharge data and constituent concentration to calibrate a regression model that describes long-term temporal change of constituent load in terms of various functions of discharge and time (Runkel et al., 2004; Duan et al., 2013; Chen et al., 2015):

$$Ln(L_t) = \beta_0 + \beta_1 Ln(Q_t) + \beta_2 Ln(Q_t)^2 + \beta_3 t + \beta_4 t_c^2 + \beta_5 \sin(2\pi t) + \beta_6 \cos(2\pi t) \quad (2)$$

where Ln is the natural logarithm function; Q_t is daily average river discharge for a given monitoring date ($m^3\ s^{-1}$), L_t is the measured daily TP load (kg P d^{-1}), which is estimated by multiplying measured TP concentration by Q_t; t is the decimal time for the corresponding monitoring date; t_c is the center of decimal time for the study period (a constant); $\beta_0 \ldots \beta_6$ are the fitted parameters in the multiple regression; β_1 and β_2 describe the relation between load and discharge; β_3 and β_4 describe the relationship between load and time; and β_5 and β_6 describe seasonal variation in load data.

In this study, the unknown parameters (i.e., $\beta_0 \ldots \beta_6$) were optimized by Akaike information criterion and Schwarz criteria (Duan et al., 2013; Huang et al., 2014) for various LOADEST formats using EViews software (version 6, Quantitative Micro Software Inc., Irvine, CA, USA). Among the various formats of LOADEST regressions (Runkel et al., 2004), Eq. (2) provided the best Akaike information criterion and Schwarz criterion (Duan et al., 2013). The calibrated LOADEST model exhibited a low average relative error and high R^2 and Nash–Sutcliffe efficiency, as well as independence of model residuals with input variables as indicated by a Durbin–Watson statistic of 1.53 (Alkorta et al., 2000) (Supplementary material: Table S1), implying that it can be reasonably applied to estimate monthly and annual riverine TP loads.

2.5. Riverine TP source apportionment

The calibrated model parameters derived for each time interval over the past 31 years were applied to the daily river discharge data, thereby estimating annual input of TP from PS (t_P, kg P yr^{-1}) and NPS (t_N, kg P yr^{-1}):

$$t_P = \sum_{i=1}^{365} AQ_i^B \quad \text{and} \quad t_N = \sum_{i=1}^{365} CQ_i^D. \quad (3)$$

As mentioned above, t_P from Eq. (3) will underestimate the original PS TP input load, since the remobilized P load that is derived from PS and previously retained in the stream channel during the low flow regime is increased with increasing river discharge and estimated as a contribution from NPS. In this study, we adopted a simple method to adjust for this underestimation. First, we assume that the average TP:Cl^- ratio from sewage is constant over a given time interval (Neal et al., 2005; Jarvie et al., 2012; Ding et al., 2014). Second, average daily Cl^- load during the low flow regime represents the original input load (Cl_O) from sewage (no significant dilution effect and runoff input) (Neal et al., 2005; Jarvie et al., 2012). Third, average daily PS TP load estimated from Eq. (1) for the high flow regime (0–10% percentile, Chen et al., 2012) represents the original input load (TP_O, kg P d^{-1}) from sewage (no physical or biological retention). Finally, the daily deposited PS P load (T_D, kg P d^{-1}) during the low flow regime (with no remobilization) can be estimated as follows:

$$T_D = \frac{TP_O}{Cl_O} Cl_L - TP_L \quad (4)$$

where Cl_L and TP_L denote measured average daily Cl^- (kg d^{-1}) and TP (kg P d^{-1}) loads during the low flow regime, respectively. Due to significant changes in daily river discharge over time, P retention and remobilization occur alternately; thus instream retained PS P is typically remobilized within several months (Jarvie et al., 2012, 2013; Sharpley et al., 2013). Accordingly, annual deposited PS TP load (t_d, kg P yr^{-1}) was estimated as the sum of daily T_D during the low flow regime for adjusting the source apportionment as follows:

$$T_P = t_P + t_d \quad \text{and} \quad T_N = t_N - t_d \quad (5)$$

where T_P and T_N denotes annual original PS and NPS TP input loads, respectively.

In this study, the low flow regime (with no remobilization) was defined as flows having no significant correlation ($p > 0.05$) between TSS concentration and water discharge over the 31 years (flows <5 $m^3\ s^{-1}$).

The river discharge at which the estimated PS and NPS TP inputs were equal (Q_e) was calculated using the coupled A, B, C, and D parameters (Bowes et al., 2008):

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

When river discharge is less than Q_e, PS inputs dominate the TP load as compared to NPS. Conversely, NPS inputs dominate the TP load when river discharge is greater than Q_e.

3. Results and discussion

3.1. Changes in river phosphorus, chloride and total suspended solids concentrations

Although measured TP concentrations varied seasonally and annually, ranging from 0.01 to 0.18 mg P L^{-1}, annual flow-adjusted average TP concentrations increased by 16-fold in the Yongan River between 1980 and 2010 (Fig. 2a). Since 1995, the river has exceeded the critical concentration of 0.05 mg P L^{-1} as an annual average enacted to reduce the risk of excessive algal growth (Li et al., 2014). Since there were no significant trends in precipitation or river discharge ($p < 0.05$), the increase in TP concentration was primarily attributed to enhanced point (PS) and nonpoint source (NPS) P inputs due to increasing urbanization, poultry production and agricultural land (Supplementary material: Fig. S1). In spite of the large overall increase in TP concentration between 1980 and 2010, the annual flow-adjusted average TP concentration showed no significant trend ($p > 0.05$) for several time intervals within the record: 1980–1984, 1985–1990, 1991–1997, 1998–2002, and 2003–2010 (Fig. 2a). This analysis suggests that the influence of annual change in human activities on PS and NPS TP inputs is limited

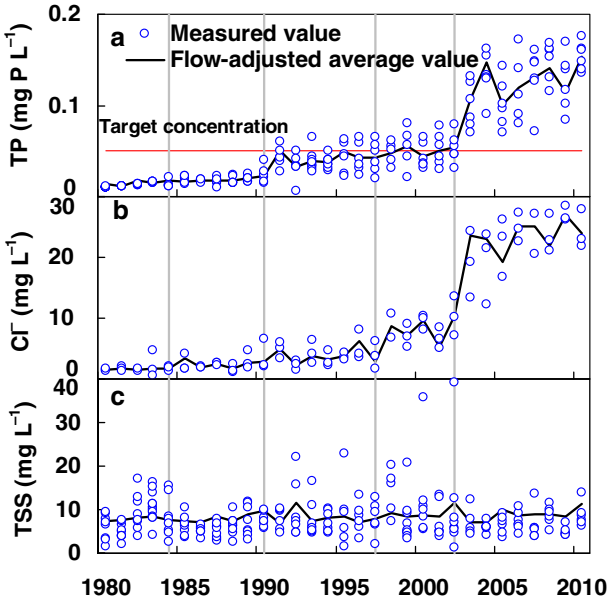


Fig. 2. Historical trends in measured concentration and flow-adjusted average concentration for TP (a), chloride during the low flow regime (<5 m^3 s^{-1}) (b), and total suspended solids (TSS) (c) in the Yongan River over the 1980–2010 period.

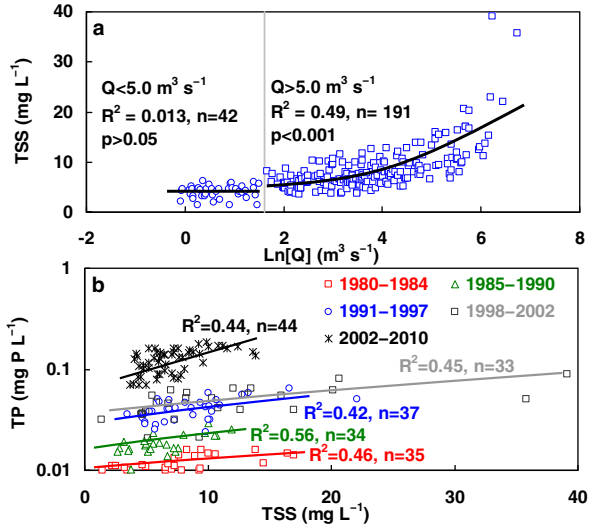


Fig. 3. Relationships between river discharge and total suspended solid (TSS) (a) and between TSS and TP in the Yongan River over the 1980–2010 period.

within each of these time intervals, supporting a primary assumption of the LAM (Bowes et al., 2008; Chen et al., 2013).

Annual flow-adjusted average Cl^- concentration during the low flow regime (water discharge <5 $m^3 s^{-1}$) ranged from 1.5 to 27.0 mg L^{-1} and increased by 20-fold between 1980 and 2010 (Fig. 2b). As a conservative indicator for wastewater (Neal et al., 2005; Jarvie et al., 2012; Ding et al., 2014), such an increasing trend for Cl^- during the low flow regime (no runoff input and limited dilution effect) implies a significant increase of PS inputs (e.g., industrial, domestic and animal wastewater). Similar to TP concentration, annual flow-adjusted average Cl^- concentration during the low flow regime showed no significant trend ($p > 0.05$) for the time intervals 1980–1984, 1985–1990, 1991–1997, 1998–2002, and 2003–2010 (Fig. 2b), indicating that the influence of annual change in human activities on PS pollution was limited within each of these time intervals. For each time interval, there were significant negative correlations observed between Cl^- concentration and river water discharge ($R^2 = 0.75–0.86$, $p < 0.01$, $n = 14–23$), further indicating that Cl^- is mainly derived from wastewater discharge during the low flow regime. Dramatic changes in both TP and Cl^- concentrations occurred between the time intervals 1998–2002 and 2003–2010 (Fig. 2a and b), which might result from increases in precipitation, agricultural land area having efficient drainage systems, and industrial activities between these two time intervals (Supplementary material: Fig. S1).

In contrast to TP and Cl^- concentrations, no significant trend was observed in flow-adjusted average total suspended solids (TSS) concentration between 1980 and 2010 ($p > 0.05$, Fig. 2c). A high correlation between TSS concentration and discharge ($R^2 = 0.44$, $p < 0.01$, Fig. 3a) suggests that land surface and channel erosion were the major drivers for temporal TSS changes. However, during the low flow regime (<5 $m^3 s^{-1}$) TSS concentrations had no significant correlation with river discharge ($p > 0.05$). This reflects the limited erosion and sediment transport potential under the low flow regime (Yu et al., 2010). Temporal changes of TP concentration were strongly related to TSS concentrations within each individual time interval ($R^2 = 0.42–0.56$, $p < 0.01$, Fig. 3b). This suggests that particle P erosion from watershed landscapes (NPS pollution) is likely the dominant source for the riverine P load, since P in wastewater effluent is generally in soluble forms (Neal et al., 2005; Sobota et al., 2011), whereas NPS P inputs will be predominantly particulate-bound (Kleinman et al., 2011; Duan et al., 2013).

3.2. Modeling of phosphorus–water discharge relationships

Based on the above analyses, we divided the 31-yr water quality record into five stable time periods (1980–1984, 1985–1990, 1991–1997, 1998–2002, and 2003–2010) for separately calibrating the LAM. The relationships between river discharge and TP concentration and load, as well as their associated model solutions, are shown in Fig. 4 and Table 1. All five time periods exhibited an increase in TP concentration, as well as TP load, with increasing river discharge, implying a dominance of NPS inputs for TP throughout the past 31 years. This deduction was supported by a predominant land use of natural vegetation (>83%) and agriculture (>10%) within the watershed (Supplementary material: Fig. S2c). Both calibrated A and C parameters increased over the 5 successive time periods, suggesting that P carried per unit water yield increased over the past 31 years. The calibrated B parameter for each time period was not equal to zero and appreciably improved the model performance, indicating that PS TP inputs were not temporally constant within each time period (Bowes et al., 2008).

The LAM provided realistic fits to the data for the 5 time periods with observed versus modeled daily river TP concentrations and loads, showing reasonably high R^2 values (>0.41 for concentration and >0.91 for load) and Nash–Sutcliffe coefficients (NS > 0.37 for concentration and >0.87 for load) (Fig. 4). These results are comparable with previous LAM applications (Bowes et al., 2008, 2009a, 2009b, 2010, 2014; Greene et al., 2011; Chen et al., 2013), as well as SWAT, AGNPS, HSPF and INCA-P applications [reviewed by Moriasi et al. (2007) and Jackson-Blake et al. (2015)], where NS > 0.20 and $R^2 > 0.20$ for daily TP concentration simulation results were considered acceptable for NPS pollution dominated watersheds. Monthly and annual riverine TP loads estimated by the LAM were further compared to those obtained with the LOADEST model (Supplementary material: Fig. S2). Close agreement observed between the results of these two models (monthly: $R^2 = 0.92$, NS = 0.91; annual: $R^2 = 0.95$, NS = 0.93) provides further validation for the efficacy of LAM in this study. Although the LAM and LOADEST model require similar input data (i.e., paired river TP concentration and water discharge records), the LOADEST model is unable to identify the independent contributions from PS and NPS. Thus, the LAM can offer accurate estimates of PS and NPS input loads with minimum data requirements and simple model structure.

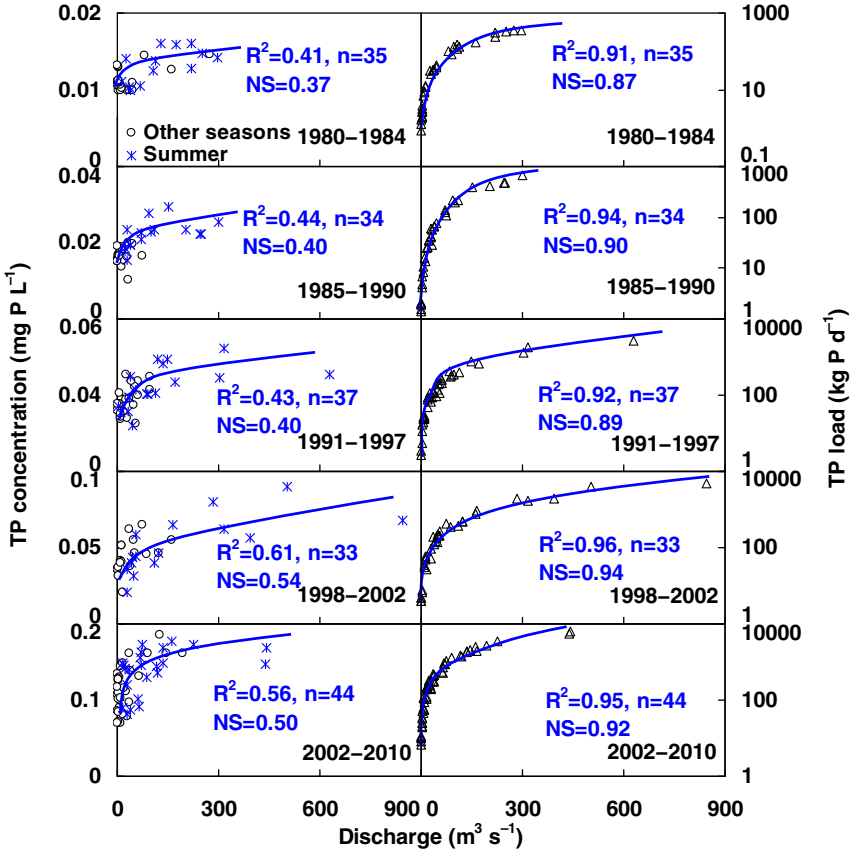


Fig. 4. Relationships between water discharge and TP concentration and load fitted by the load apportionment model for the Yongan River over the 1980–2010 period. NS denotes Nash–Sutcliffe efficiency.

3.3. Changes in annual point and nonpoint source phosphorus inputs

This study was able to estimate the instream retained P load from PS during the low flow regime (<5 $m^3 s^{-1}$, Fig. 3a) using Eq. (5). The estimated average TP:Cl^- ratio varied between 0.013 and 0.023 over the 5 time periods (Table 1), which is comparable with published values for sewage effluents (e.g., 0.007–0.044) (Neal et al., 2005; Jarvie et al., 2012). Estimated PS P load retained within the river during the low flow regime ranged from 0.8 to 35.5 Mg P yr^{-1} and accounted for 2–29% of annual riverine TP load. Both metrics exhibited an increasing trend from 1980 to 2010 (Fig. 5a, $p < 0.01$) suggesting that it should be considered in the riverine P source apportionment. The percentage contribution of the remobilized PS input to annual river TP loads decreased with increasing discharge ($R^2 = 0.51$, $p < 0.01$) or rainfall ($R^2 = 0.44$, $p < 0.01$), indicating that caution should be particularly applied in dry years when conventional LAM results may incorporate a large underestimation of PS TP inputs.

Estimated annual PS TP inputs (incorporating the retained PS TP load, which contributed 18–65% of the annual PS TP input) ranged from 2.4 to 67.2 Mg P yr^{-1} and accounted for 7–45% of annual riverine TP load (Fig. 5a). Over the past 31 years, PS TP load increased 23-fold, consistent with the 20-fold increase in flow-adjusted average Cl^- concentration during the low flow regime (Fig. 2b). A 26% increase in population and a 4.8-fold increase in poultry production (Supplementary

Table 1
The TP load apportionment model parameters for five time periods in the Yongan River watershed for the 1980–2010 period.

Parameters	Values	1980–1984	1985–1990	1991–1997	1998–2002	2003–2010
A	Mean	1.18	2.20	9.72	31.43	33.10
	5%	0.12	0.31	2.53	6.23	9.75
	95%	4.49	5.70	14.98	44.08	55.95
B	Mean	0.26	0.29	0.19	0.14	0.31
	5%	0.06	0.07	0.01	0.02	0.05
	95%	0.88	0.85	0.79	0.69	1.07
C	Mean	0.44	0.54	0.90	3.01	4.24
	5%	0.12	0.13	0.21	1.23	1.69
	95%	1.21	1.51	1.91	5.34	7.17
D	Mean	1.10	1.14	1.13	1.05	1.06
	5%	0.70	0.86	0.60	0.58	0.17
	95%	1.50	1.41	1.66	1.44	1.85
Q_e ($m^3 s^{-1}$)		3.2	5.2	12.5	14.8	15.5
Average Cl^- load in the low flow regime (kg d^{-1})		536	750	1357	3776	6659
Average point source TP load in the high flow regime (kg d^{-1})		6.8	12.5	29.2	71.4	151.9

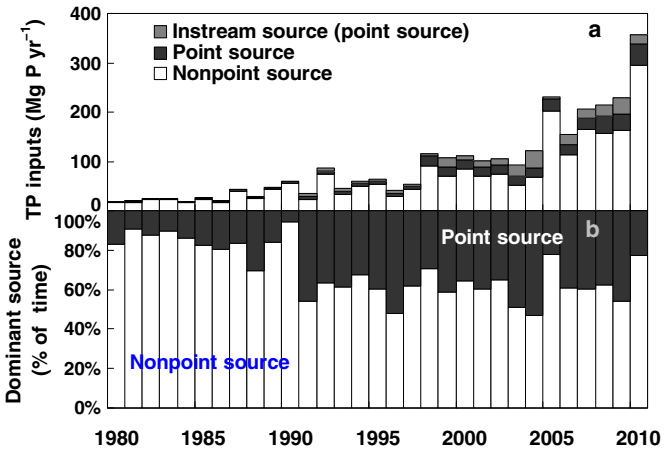


Fig. 5. Annual point and nonpoint source TP input loads (a) and point and nonpoint source pollution dominated time percentages (b) for the Yongan River over the 1980–2010 period.

material: Fig. S1b) imply a considerable increase in domestic and animal wastewater discharge. In terms of field investigations, a considerable proportion of household wastewaters in residential areas is directly discharged into the drainage system and effectively operates as numerous small PS sewage inputs. Although no detailed data for industrial sewage were available, a 200-fold increase in industrial gross domestic production (Supplementary material: Fig. S1b) implies a potential increase in industrial PS TP input. In many watersheds in eastern China, only slow progress is being made to fully capture and treat these widely distributed PS (Chen et al., 2013). The LAM is thus a potentially powerful tool for evaluating changes in sewage nutrient discharge after implementation and enhancement of sewage treatment, resulting in considerable savings in monitoring costs.

Estimated annual NPS TP inputs ranged from 15.6 to 294.1 Mg P yr^{-1} and accounted for 55–93% of annual riverine TP load, implying the dominant role of NPS pollution (Fig. 5a). This is supported by strong correlation between riverine TP and TSS concentrations (Fig. 3a), as well as positive correlations between TP concentration and river discharge within each of the investigated time periods (Fig. 4). Although P fertilizer application increased by 1.5-fold from 1980 to 1999 and then decreased by 37% from 2000 to 2010 (Supplementary material: Fig. S2b), NPS TP inputs continuously increased by ~19-fold over the past 31 years, implying the increasing contribution of legacy P sources (Basu et al., 2010; Sharpley et al., 2013, 2015). This is supported by an average 2.0-fold increase in TP concentration ($n = 209$) and an average 1.4-fold increase in Olsen-P concentration ($n = 406$) measured in the upper 20-cm layer of agricultural soils between 1984 and 2009 in the Yongan River watershed (Chen et al., 2015). As a result, the P concentration of eroded sediments increased (with no increase in TSS between 1980 and 2010, Fig. 2c), since fine soil particles having a greater P content can be transported preferentially via erosion (Puustinen et al., 2007). Increasing NPS P inputs may also be associated with increasing agricultural land area having efficient drainage systems ($R^2 = 0.47$, $p < 0.01$) and increasing developed land area ($R^2 = 0.46$, $p < 0.01$) (Supplementary material: Fig. S2c). An increase in hydrologic connectivity via efficient drainage enhances P delivery from land to river due to decreased water residence time and filtering capacity with the watershed (Gentry et al., 2007; Jarvie et al., 2013). The developed land area decreases P retention and enhances flushing during rainfall events due to greater impervious surface area (Sobota et al., 2011; Chen et al., 2015).

According to the estimated river discharge value at which PS and NPS TP inputs to the river are equal (Table 1), the percentage of time that NPS dominates was 53–95%, while PS dominates 5–47% of the time (Fig. 5b). The amount of time dominated by PS increased 1.8-fold over the 31-yr record and was increased by decreasing river discharge ($R^2 = 0.32$, $p < 0.05$) or rainfall ($R^2 = 0.29$, $p < 0.05$). Therefore, although NPS pollution dominates the overall TP load and should be targeted for river TP pollution mitigation, PS management should not be ignored, especially during dry years.

3.4. Point and nonpoint source phosphorus inputs during the critical summer period

Environmental managers are often required to preferentially focus on nutrient pollution during the sensitive summer period with enhanced potential for algae growth (Bowes et al., 2008, 2009a). Lakes, reservoirs, and estuaries in eastern China have the highest risk for eutrophication during the summer when high rainfall generates high nutrient inputs and high temperatures and sunlight stimulate algae growth (Chen et al., 2013; Huang et al., 2014). In the Yongan River watershed, cumulative river water yield and TP load during the summer high-flow period (May to October) accounted for 60–80% and 64–87% of annual total water yield and TP load, respectively (Fig. 6a). Therefore, the summer high-flow season is the most important period for targeting riverine P load reduction for the NPS pollution dominated watersheds in eastern China.

Due to enhanced NPS inputs and remobilization of retained PS TP by frequent high flow events, the summer season generally has higher TP concentrations than other seasons (Fig. 4). The PS (incorporating the channel-retained PS TP load from the low flow regime) and NPS TP inputs accounted for 3–40% and 60–97% of the riverine TP load during the summer, respectively (Fig. 6b). The percentage of time that NPS and PS pollution dominates the TP load was 59–97% and 3–41%, respectively (Fig. 6c). These results clearly indicate the necessity for targeting NPS TP reduction to control the summer eutrophication risk. However, a considerable proportion of NPS TP inputs may be attributed to legacy P that has accumulated in soils, wetlands, and riparian buffers or even groundwater from historical anthropogenic P inputs in previous years (Sharpley et al., 2013; Chen et al., 2015). The occurrence of legacy P sources implies that contemporary P source reductions would result in a limited decrease in NPS P input load to rivers (Meals et al., 2010; Sharpley et al., 2013). Therefore, adopting and improving interception measures (e.g., buffer strips, constructed wetlands) within the watershed would provide a more immediate reduction in NPS P loads compared to source reduction measures (Basu et al., 2010). Such interception measures are more pronounced for slowing water runoff

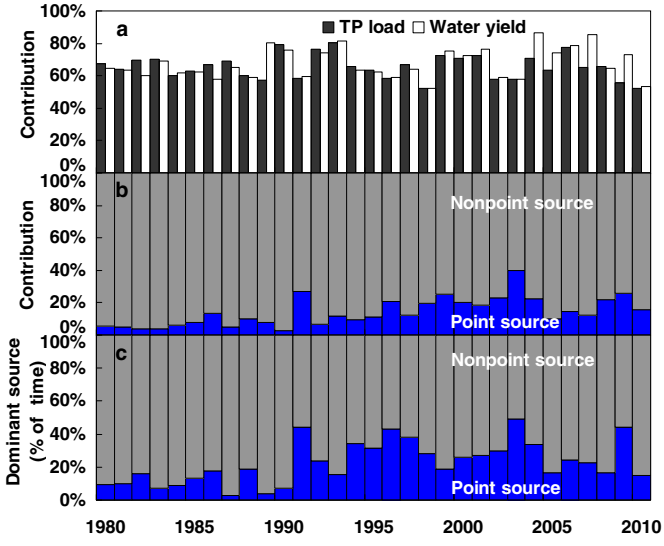


Fig. 6. Contributions of cumulative water yield and TP load in summer (May to October) to annual amounts (a), point and nonpoint source contributions to riverine TP load (b) and point and nonpoint source pollution dominated time percentages (c) in summer for the Yongan River over the 1980–2010 period.

and trapping sediment and P in the summer growing season. Thus, they are more effective for reducing higher NPS P loads during the summer high-flow period.

The summer PS TP input and PS-dominated time period increased by 1.8-fold and 1.2-fold over the past 31 years, respectively (Fig. 6), emphasizing the increasing importance of PS pollution to riverine P loads. Compared to particle P, soluble P from PS inputs may be more bioavailable to algae (Neal et al., 2005; Bowes et al., 2008, 2009a). In contrast to NPS control, PS pollution can be mitigated more easily and efficiently through implementing and improving industrial, domestic, and animal sewage collection/treatment. Therefore, reducing PS P loads should be increasingly adopted to for immediate reduction in riverine P levels during the critical summer season.

3.5. Model comparisons and implications

The LAM is particularly useful for regions having limited available data for calibrating other watershed models. Once the LAM has been calibrated to produce an acceptable fit to the river monitoring record, the empirically-fitted model parameters can be applied to analyze high temporal-resolution river discharge data, which is difficult to achieve with typical lumped models that usually operate on an annual time step (Chen et al., 2013). Such temporal resolution is critical for application to the most sensitive times of the year when eutrophication is most likely to occur (Bowes et al., 2008, 2009a, 2009b). Although it cannot directly identify the individual contribution from specific nutrient sources (e.g., sewage treatment discharge, fertilizer application, animal and domestic wastes), an important advantage of the LAM is that it avoids the uncertainty derived from the lag effect of legacy phosphorus sources on NPS TP entering rivers, which has been widely observed in field- and watershed-scale studies (Basu et al., 2010; Sharpley et al., 2013, 2015; Jarvie et al., 2013; Chen et al., 2015). The lag effect has not been strictly addressed in the majority of current watershed models, resulting in considerable uncertainty in estimating NPS pollution loads (Meals et al., 2010; Kleinman et al., 2011).

Compared to conventional LAM applications, this study explicitly addressed instream retention/remobilization of the PS P load. This was accomplished by taking the ratio of the PS TP input load during the high flow regime (no retention) and Cl^- load measured during the low flow regime (when erosion is limited) as a proxy for the average TP:Cl^- ratio of the original PS inputs at each time interval (Neal et al., 2005; Jarvie et al., 2012). Considering the difficulty in obtaining TP:Cl^- ratios for all sewage inputs for a large watershed, it offers a simple and applicable method to address the uncertainty in estimating PS and NPS TP inputs from LAMs, as well as other watershed models. In addition to water discharge, instream phosphorus remobilization is regulated by other factors (e.g., temperature and anoxic conditions, Hayakawa et al., 2015). Additional field studies are required for developing quantitative relationships between influencing factors and phosphorus remobilization, which can be applied to modify many current models. In contrast to conventional LAM applications, this study further adopted a LOADEST model that requires minimal river monitoring data for estimating monthly and annual riverine nutrient loads over a long-term time series (Runkel et al., 2004; Duan et al., 2013; Chen et al., 2015). This approach offers an effective tool for verifying LAM results for watersheds where long-term records on nutrient sources and land use, as well as export coefficients, are unavailable for applying to lumped models.

Conventional LAM application to long-term time series generally divides the data into several 5-yr intervals to separate potential temporal changes in anthropogenic interventions (e.g., establishing or improving sewage treatment). In contrast, this study statistically divided the 31-yr time series into five uneven time periods (Fig. 2) based on changes in the annual flow-adjusted average TP concentrations, as well as Cl^- concentration during the low flow regime, offering a more realistic fit to model assumptions. As a conservative indicator for sewage (Jarvie et al., 2012; Ding et al., 2014), information on riverine Cl^- concentration is useful to verify long-term changes in estimated PS TP inputs from LAMs, as well as other watershed models. A monthly to bimonthly monitoring interval, which is typical of many monitoring programs (Shrestha et al., 2008; Yu et al., 2010; Chen et al., 2013), may not adequately characterize the high-flow events due to their limited occurrence throughout a given year (Johnes, 2007). Although multiple-year river monitoring datasets (>5 years) can generally offset the insufficiency of a monthly sampling interval for capturing high-flow events (Bowes et al., 2009a; Chen et al., 2013), more frequent water quality monitoring efforts are necessary to improve the LAM accuracy, as well as the overall knowledge required for effective water quality management.

4. Conclusion

This study presents the first historically-explicit quantification of point (PS) and nonpoint source (NPS) TP inputs to a typical river in eastern China that has undergone tremendous economic development in the last three decades using a load apportionment model (LAM). Compared with conventional LAM applications, this study advanced the modeling approach through explicitly addressing the instream retention/remobilization component of the PS P load and efficiently verifying model results using output from the LOADEST model. In addition, the long-term (31 year) time series was objectively divided into several distinct time periods according to changes in observed annual flow-adjusted average TP concentrations and Cl^- concentration during the low flow regime (a proxy for wastewater inputs). These time periods provided a temporally-explicit calibration of the LAM, offering a more realistic fit to the model assumption (i.e., annual changes in PS and NPS inputs are mainly determined by hydrological conditions). Based on our analysis, in the Yongan River watershed TP pollution control strategies should be preferentially focused on NPS reductions, especially during the summer high-flow period when the greatest eutrophication risk occurs. Point source reduction of TP will become increasingly more important, especially since these P inputs are generally more available to algae.

Acknowledgments

We thank the local government for providing data critical for this investigation. This work was supported by the National Natural Science Foundation of China (41371010) and Zhejiang Provincial Natural Science Foundation of China (LY13D010002).

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2015.06.079.

References

Alkorta, I., Barrios, L., Rozas, I., Elguero, J., 2000. Comparison of models to correlate electron density at the bond critical point and bond distance. J. Mol. Struct.-Teochem. 496, 131–137.

Basu, N.B., Destouni, G., Jawitz, J.W., Thompson, S.E., Loukinova, N.V., Darracq, A., Zanardo, S., Yaeger, M., Sivapalan, M., Rinaldo, A., Rao, P.S.C., 2010. Nutrient loads exported from managed catchments reveal emergent biogeochemical stationarity. Geophys. Res. Lett. 37, L23404.

Bowes, M.J., Smith, J.T., Jarvie, H.P., Neal, C., 2008. Modelling of phosphorus inputs to rivers from diffuse and point sources. Sci. Total Environ. 395, 125–138.

Bowes, M.J., Smith, J.T., Jarvie, H.P., Neal, C., Barden, R., 2009a. Changes in point and diffuse source phosphorus inputs to the River Frome (Dorset, UK) from 1966 to 2006. Sci. Total Environ. 407, 1954–1966.

Bowes, M.J., Smith, J.T., Neal, C., 2009b. The value of high-resolution nutrient monitoring: a case study of the River Frome, Dorset, UK. J. Hydrol. 378, 82–96.

Bowes, M.J., Neal, C., Jarvie, H.P., Smith, J.T., Davies, H.N., 2010. Predicting phosphorus concentrations in British rivers resulting from the introduction of improved phosphorus removal from sewage effluent. Sci. Total Environ. 408, 4239–4250.

Bowes, M.J., Jarvie, H.P., Naden, P.S., Old, G.H., Scarlett, P.M., Roberts, C., et al., 2014. Identifying priorities for nutrient mitigation using river concentration–flow relationships: the Thames basin, UK. J. Hydrol. 517, 1–12.

Bowes, M.J., Jarvie, H.P., Halliday, S.J., Skeffington, R.A., Wade, A.J., Loewenthal, M., Gozzard, E., Newman, J.R., Palmer-Felgate, E.J., 2015. Characterising phosphorus and nitrate inputs to a rural river using high-frequency concentration–flow relationships. Sci. Total Environ. 511, 608–620.

Chen, D.J., Dahlgren, R.A., Shen, Y.N., Lu, J., 2012. A Bayesian approach for calculating variable total maximum daily loads and uncertainty assessment. Sci. Total Environ. 430, 59–67.

Chen, D.J., Dahlgren, R.A., Lu, J., 2013. A modified load apportionment model for identifying point and diffuse source nutrient inputs to rivers from stream monitoring data. J. Hydrol. 501, 25–34.

Chen, D.J., Huang, H., Hu, M.P., Dahlgren, R.A., 2014. Influence of lag effect, soil release, and climate change on watershed anthropogenic nitrogen inputs and riverine export dynamics. Environ. Sci. Technol. 48, 5683–5690.

Chen, D.J., Hu, M.P., Guo, Y., Dahlgren, R.A., 2015. Influence of legacy phosphorus, land use, and climate change on anthropogenic phosphorus inputs and riverine export dynamics. Biogeochemistry 123, 99–116.

Ding, J.T., Xi, B.D., Gao, R.T., He, L.S., Liu, H.L., Dai, X.L., Yu, Y.J., 2014. Identifying diffused nitrate sources in a stream in an agricultural field using a dual isotopic approach. Sci. Total Environ. 484, 10–18.

Duan, W., Takara, K., He, B., Luo, P., Nover, D., Yamashiki, Y., 2013. Spatial and temporal trends in estimates of nutrient and suspended sediment loads in the Ishikari River, Japan, 1985 to 2010. Sci. Total Environ. 461–462, 499–508.

Freedman, P.L., Shabman, L., Reckhow, K., 2008. Don't debate; adaptive implementation can help water quality professionals achieve TMDL goals. Water Environ. Technol. 20, 1023–1031.

Gentry, L.E., David, M.B., Royer, T.V., Mitchell, C.A., Starks, K.M., 2007. Phosphorus transport pathways to streams in tile-drained agricultural watersheds. J. Environ. Qual. 36, 408–415.

Greene, S., Taylor, D., McElarney, Y.R., Foy, R.H., Jordan, P., 2011. An evaluation of catchment-scale phosphorus mitigation using load apportionment modelling. Sci. Total Environ. 409, 2211–2221.

Hayakawa, A., Ikeda, S., Tsushima, R., Ishikawa, Y., Hidaka, S., 2015. Spatial and temporal variations in nutrients in water and riverbed sediments at the mouths of rivers that enter Lake Hachiro, a shallow eutrophic lake in Japan. Catena. http://dx.doi.org/10.1016/j.catena.2015.04.009.

Huang, H., Chen, D.J., Zhang, B.F., Zeng, L.Z., Dahlgren, R.A., 2014. Modeling and forecasting riverine dissolved inorganic nitrogen export using anthropogenic nitrogen inputs, hydroclimate, and land-use change. J. Hydrol. 517, 95–104.

Jackson-Blake, L.A., Dunn, S.M., Helliwell, R.C., Skeffington, R.A., Stutter, M.I., Wade, A.J., 2015. How well can we model stream phosphorus concentrations in agricultural catchments? Environ. Modell. Software 64, 31–46.

Jarvie, H.P., Sharpley, A.N., Scott, J.T., Haggard, B.E., Bowes, M.J., Massey, L.B., 2012. Within-river phosphorus retention: accounting for a missing piece in the watershed phosphorus puzzle. Environ. Sci. Technol. 46, 13284–13292.

Jarvie, H.P., Sharpley, A.N., Withers, P.J.A., Scott, J.T., Haggard, B.E., Neal, C., 2013. Phosphorus mitigation to control river eutrophication: Murky waters, inconvenient truths and 'post-normal' science. J. Environ. Qual. 42, 295–304.

Johnes, P.J., 2007. Uncertainties in annual riverine phosphorus load estimation: impact of load estimation methodology, sampling frequency, baseflow index and catchment population density. J. Hydrol. 332, 214–258.

Kleinman, P.J.A., Sharpley, A.N., McDowell, R.W., Flaten, D.N., Buda, A.R., Tao, L., Bergstrom, L., Zhu, Q., 2011. Managing agricultural phosphorus for water quality protection: principles for progress. Plant Soil 349, 169–182.

Li, M.T., Xu, K.Q., Watanabe, M., Chen, Z.Y., 2007. Long-term variations in dissolved silicate, nitrogen, and phosphorus flux from the Yangtze River into the East China Sea and impacts on estuarine ecosystem. Estuar. Coast. Shelf Sci. 71, 3–12.

Li, Y.Y., Meng, C., Gao, R., Yang, W., Jiao, J.X., Li, Y., Wang, Y., Wu, J.S., 2014. Study on phosphorus loadings in ten natural and agricultural watersheds in subtropical region of China. Environ. Monit. Assess. 186, 2717–2727.

Liu, S., Zhang, J., Chen, H., Wu, Y., Xiong, H., Zhang, Z., 2003. Nutrients in the Changjiang and its tributaries. Biogeochemistry 62, 1–18.

Meals, D.W., Dressing, S.A., Davenport, T.E., 2010. Lag time in water quality response to best management practices: a review. J. Environ. Qual. 39, 85–96.

Moriasi, D.N., Arnold, J.G., Van Liew, M.W., Bingner, R.L., Harmel, R.D., Veith, T.L., 2007. Model evaluation guidelines for systematic quantification of accuracy in watershed simulations. Trans. ASABE 50, 885–900.

Neal, C., Jarvie, H.P., Neal, M., Love, A.J., Hill, L., Wickham, H., 2005. Water quality of treated sewage effluent in a rural area of the upper Thames Basin, southern England, and the impacts of such effluents on riverine phosphorus concentrations. J. Hydrol. 304, 103–117.

Puustinen, M., Tattari, S., Koskiaho, J., Linjama, J., 2007. Influence of seasonal and annual hydrological variations on erosion and phosphorus transport from arable areas in Finland. Soil Tillage Res. 93, 44–55.

Runkel, R.L., Crawford, C.G., Cohn, T.A., 2004. Load estimator (Loadest): a Fortran program for estimating constituent loads in streams and rivers. U.S. Geological Survey Techniques and Methods Book 4, Chapter A5. U.S. Geological Survey, Reston.

Schaffner, M., Bader, H.P., Scheidegger, R., 2009. Modelling the contribution of point-source and non-point-source pollution to the Thachin River. Sci. Total Environ. 407, 4902–4915.

Sharpley, A.N., Jarvie, H.P., Buda, A., May, L., Spears, B., Kleinman, P., 2013. Phosphorus legacy: overcoming the effects of past management practices to mitigate future water quality impairment. J. Environ. Qual. 42, 1308–1326.

Sharpley, A.N., Bergström, L., Aronsson, H., Bechmann, M., Bolster, C.H., Börling, K., Djodjic, F., Jarvie, H.P., Schoumans, O.F., Stamm, C., Tonderski, K.S., Ulén, B., Uusitalo, R., Withers, P.J., 2015. Future agriculture with minimized phosphorus losses to waters: research needs and direction. Ambio 44, 163–179.

Shrestha, S., Kazama, F., Newham, L.T.H., 2008. A framework for estimating pollutant export coefficients from long-term in-stream water quality monitoring data. Environ. Model Softw. 23, 182–194.

Sobota, D.J., Harrison, J.A., Dahlgren, R.A., 2011. Linking dissolved and particulate phosphorus export in rivers draining California's Central Valley with anthropogenic sources at the regional scale. J. Environ. Qual. 40, 1290–1302.

Yang, L.P., Han, J.P., Xue, J.L., Zeng, L.Z., Shi, J.C., Wu, L.S., Jiang, Y.H., 2013. Nitrate source apportionment in a subtropical watershed using Bayesian model. Sci. Total Environ. 463, 340–347.

Yu, T., Meng, W., Ongley, E., Li, Z.C., Chen, J.S., 2010. Long-term variations and causal factors in nitrogen and phosphorus transport in the Yellow River, China. Estuar. Coast. Shelf Sci. 86, 345–351.