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Long-term riverine nitrogen dynamics reveal the efficacy of water pollution control strategies

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ABSTRACT

Identification of long-term water quality trends in response to watershed anthropogenic interventions is crucial for developing and adapting water pollution control strategies. This study represents the first use of the Weighted Regressions on Time, Discharge, and Season (WRTDS) model to evaluate trends and sources of riverine nitrogen (N) levels over the 1980–2019 period in the Yongan River watershed of eastern China. The WRTDS model showed satisfactory accuracies for predicting daily riverine total N (TN), NH_4^+ and NO_3^- concentrations/loads ($R^2 > 0.55$, n = 366). Modeled flow-normalized riverine NH_4^+ concentration increased by 789% from 1980 to 2009 and then decreased by 63% in 2010–2019. This changing trend for riverine NH_4^+ concentration was mainly attributed to a 43% decrease of wastewater NH_4^+ discharge load in 2010–2019 due to establishment of three new WWTPs in urban areas and enhanced rural domestic sewage collection/treatment. Although chemical N fertilizer use decreased by 49% and domestic animal numbers decreased by 73% in 2000–2019, flow-normalized riverine TN and NO_3^- concentrations progressively increased by 161% and 232% in 1980–2019, respectively. The paradox between decreasing N inputs and increasing riverine TN/NO_3^- concentrations is attributed to inputs of legacy N from soil and groundwater. This is supported by the 3.8-fold increase of riverine NO_3^- concentration in 1980–2019 (86% increase in 2000–2019) following 10-days with no-precipitation (representing groundwater contributions to baseflow) and a 4.1-fold increase of riverine NO_3^- concentration in 1980–2019 (91% increase in 2000–2019) following the first rainstorm after 10-days of no-precipitation (representing soil flushing). These results document that point-source pollution control efforts were effective, whereas benefits from nonpoint-source pollution control were masked by inputs from legacy N pollution. The WRTDS model was demonstrated to be a useful tool for assessing long-term riverine N pollution dynamics and sources, thereby providing decision-makers with critical information to guide watershed N pollution control strategies.

1. Introduction

Excessive nitrogen (N) inputs originating from anthropogenic activities have caused sharp increases in N loadings to surface waters worldwide, leading to degradation of aquatic ecosystem health, harmful algal bloom and hypoxia/anoxia (Galloway et al., 2008; Gu et al., 2015). Over the past several decades, many regions and/or countries have made tremendous efforts (e.g., improving domestic wastewater treatment, reducing fertilizer applications, and recycling domestic animal wastes) to mitigate aquatic N pollution (Bernhardt et al., 2005; Craig et al., 2008; Ma et al., 2020; Stets et al., 2020). However, it is critical to monitor the water quality changes to evaluate the effectiveness of these control actions (Lee et al., 2016; Liu et al., 2017; Sinha and Michalak, 2016). Due to a lag time between implementation of watershed management measures and the river water quality response, long-term water quality trend analysis is required to fully explore the efficiency of relevant N pollution control efforts (Meals et al., 2010).

In general, riverine N concentration or load metrics display high daily, seasonal and annual variability due to the interaction of natural (e.g., climate and hydrology) and anthropogenic factors (e.g., N input

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density and land use) (Chen et al., 2004; Choquette et al., 2019; Sinha and Michalak, 2016; Stets et al., 2020). In addition, riverine N monitoring data are usually discrete and/or sampled with variable intervals, such as monthly, biweekly or weekly (Hirsch et al., 2010). Therefore, appropriate statistical approaches are required to detect long-term trends in riverine N levels based on discrete monitoring data and to identify the influence of anthropogenic interventions (Stenback et al., 2011). A range of statistical approaches, such as nonparametric Mann-Kendall test (Kendall, 1975), Sen's slope (Sen, 1968), seasonal Sen's slope (Hirsch et al., 1982), generalized additive (GAM) model (Morton and Henderson, 2008), LOAD ESTimator (LOADEST) model (Runkel et al., 2004) and Weighted Regressions on Time, Discharge, and Season (WRTDS) model (Hirsch et al., 2010) are utilized to quantify trend magnitude changes in riverine N and other water quality indexes (P, sediment, carbon, etc.). From a long-term perspective, watershed pollution sources, land-use types and distributions, and hydrometeorological patterns are remarkably altered, thereby imposing variable relationships between river water quality and hydrology over time (Hirsch et al., 2010). Among the above-mentioned statistical approaches, WRTDS utilizes a window regression approach for each day of the estimation period, which provides variable coefficients for quantifying changes in water quality trends over long-term periods (Hirsch et al., 2010). Thus, the WRTDS model provides a flexible, theoretically robust, and applicable tool to quantify long-term water quality trends over a broad range of conditions (Hirsch, 2014; Lee et al., 2016).

As a conceptually-rooted weighted regression model, WRTDS comprehensively describes characteristics and trends of water quality signals throughout the discharge and time regimes based on discrete monitoring data, as well as distinguishing anthropogenic and climate impacts, with the "flow-normalization" procedure (Hirsch et al., 2010; Hirsch and De Cicco, 2015). Integrating historical information concerning anthropogenic activities with the WRTDS can provide critical evidence for identifying the roles of different components (e.g., point/nonpoint sources of pollution, surface water and groundwater) regulating riverine water quality trends (Hirsch et al., 2010; Zhang et al., 2021). Therefore, WRTDS has been widely applied for assessing water-quality trends and sources in the Mississippi River watershed (Sprague et al., 2011), Susquehanna River basin (Van Meter et al., 2017), South Fork Shenandoah River (Zhang et al., 2021), and Grand River watershed (Van Meter and Basu, 2017). However, the WRTDS model has not been evaluated to address long-term riverine N level trend analyses in China, a country with rapidly changing and severe riverine N pollution levels originating from multiple point and nonpoint sources. Rare works are available to address long-term riverine N dynamics in response to multiple water pollution control measures.

Over the past several decades, many Chinese rivers (e.g., the Yangzi River, Yellow River and Pearl River) have experienced significant water quality impairment associated with rapid economic development, human population expansion, urbanization and agricultural intensification (Chen et al., 2004; Chen et al., 2019; Gao et al., 2016; Huang et al., 2021). To control water pollution, the Chinese government has implemented a range of national-level measures (Zhang and Wen, 2008; Ma et al., 2020), such as Regulation on the Prevention and Control of Pollution from Large-Scale Breeding of Livestock and Poultry (2014), Action Plan for Water Pollution Prevention and Control (2015), Action Plan for Zero Growth in Fertilizer Use (2015) and Toilet Revolution Plan (2015). In compliance with national policies, some local governments issued and implemented more rigorous water pollution control measures. For example, Zhejiang Province carried out the "811" (eight major river systems and eleven key supervised areas) Environmental Pollution Renovation Activity since 2005 and the Five Water (Wastewater, Floodwater, Waterlogging, Water supply and Water saving) Co-treatment Program since 2014. To assess the efficacy of these efforts, several national or regional assessments of selected rivers and lakes have documented improvements in water quality in recent years (Huang et al., 2021; Liu et al., 2017; Ma et al., 2020). These assessments usually addressed water quality trends based on analyses of often limited and/or short-term monitoring records, rendering them unable to identify the efficiencies of individual water pollution control efforts (e.g., extending and improving WWTPs, adopting fertilizer reduction strategy, restricting livestock populations) (Huang et al., 2021; Ma et al., 2020). Therefore, it is strongly warranted to investigate long-term river water quality trends to identify the efficacies of different water pollution control measures to guide future watershed management.

Herein, this study represents the first use of the WRTDS model to address long-term riverine N dynamics in a typical river system (the Yongan River) in eastern China. Based on a 40-year record (1980–2019) of riverine N (TN, NO_3^- and NH_4^+) concentrations and river discharge, the WRTDS model was calibrated to address long-term riverine N dynamics. Our specific objectives were to investigate (1) the applicability of the WRTDS model, (2) the trends and sources of riverine N pollution, and (3) the efficacy of point and nonpoint source pollution control efforts. This work assesses long-term riverine N dynamics in response to multiple water pollution control measures, thereby guiding the development/optimization of N management strategies to effectively control excessive riverine N levels to downstream coastal waters.

2. Method

2.1. Watershed description

The Yongan River watershed (120° 13′ 46″–121° 0′ 52″E and 28° 28′ 10″–29° 2′ 22″N; elevation ~ 15–1000 m) is located in the highly developed Taizhou area of Zhejiang Province in eastern China (Fig. 1). It is the third largest river of Zhejiang Province (one of eight major river systems in Zhejiang Province) and flows into Taizhou Estuary and the East China Sea, a coastal area that commonly experiences hypoxia (Gao and Zhang, 2010; Li et al., 2007). 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} at the sampling location. The climate is subtropical monsoon having average annual precipitation of 1400 mm and an average annual temperature of 17.4 °C. Rainfall mainly occurs in May–September with a typhoon season in July–September and a dry season from October to February. There are no dams or transboundary water withdrawals along the main river channel and no significant trends in annual precipitation amount or average river discharge during the study period (Table 1). Total population within the watershed increased from ~590,000 to ~770,000 between 1980 and 2019. Agricultural land (including paddy field, garden plot and dry land) accounted for 11–17% of total watershed area in 1980–2019, with developed land (including rural/urban residential lands, roads and mining/industrial lands), woodland, and barren land contributing to 2–5%, 68–72%, and 6–17%, respectively (Table 1).

To comply with the "811" Environmental Pollution Renovation Activity (2005) and "Five Water Co-treatment Program" (2014) issued by Zhejiang Province, the Taizhou City government implemented a range of measures (e.g., urban and rural infrastructure construction, industrial wastewater treatment, livestock and poultry breeding regulation, application of formula fertilization by soil testing) to mitigate water pollution (Wanting, 2017). In the Yongan River watershed, three new centralized WWTPs were established (one in 2007 and two in 2010) to treat domestic wastewater and selected industrial wastewaters in urban areas. Total sewage treatment capacity in the urban area was increased to 4.8 × 10^4 ton day^{-1} with anaerobic–anoxic–oxic treatment process, resulting in a reduction of the annual total NH_4^+ load in wastewater discharge by ~ 43% between 2010 and 2019 (Fig. 2). Beginning in 2005, industrial enterprises not connected to centralized WWTPs were required to develop independent sewage treatment facilities to meet category I integrated wastewater discharge standards (GB 8978–1996). In rural areas, each village (~500 in the watershed) developed a domestic sewage centralized treatment facility with a capacity of at least

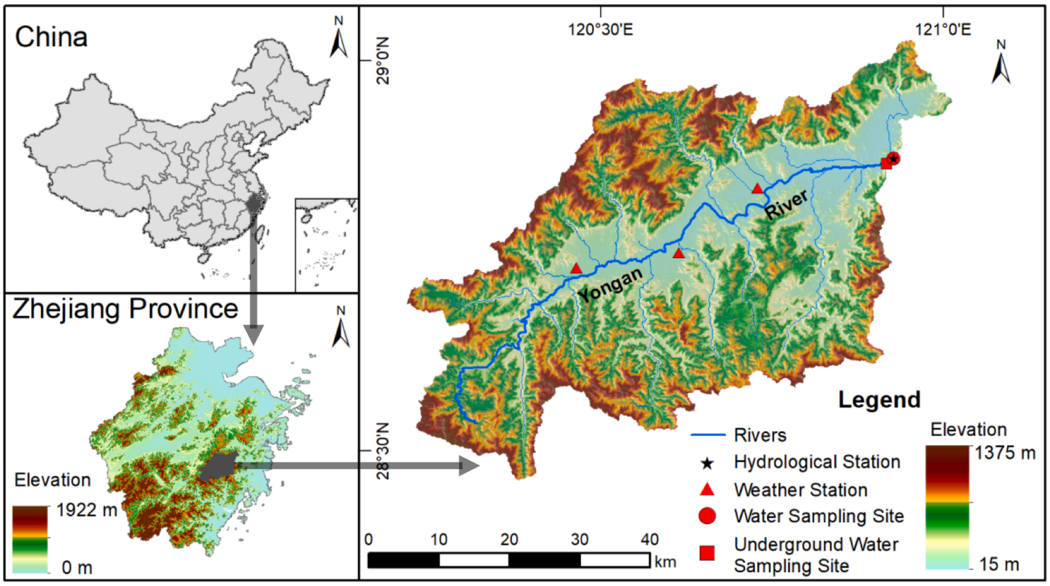

Fig. 1. Location of Yongan River Basin in China and Zhejiang Province along with the water quality sampling site and weather stations.

Table 1
Characteristics of land-use distribution, hydroclimate, population, domestic animal production and riverine N concentrations for the Yongan River watershed over the 1980–2010 period.

Periods	1980 s	1990 s	2000 s	2010 s
Agricultural land (%)	11	11	13	17
Developed land (%)	2	3	3	5
Forest (%)	68	68	67	72
Barren land (%)	18	18	17	6
Precipitation (m year^{-1})	1.37	1.42	1.42	1.65
River water average discharge (m^3 s^{-1})	72.2	77.5	70.7	77.4
CV of discharge (Unitless)	2.04	2.59	2.69	2.30
Population density (capita km^{-2})	248	266	288	306
Domestic livestock production (ton year^{-1})	1403	1172	787	508
Poultry production (ton year^{-1})	76	158	225	242
Mean TN concentration (mg N L^{-1})	0.92	1.07	1.38	2.18
Mean NH_4^+ concentration (mg N L^{-1})	0.07	0.07	0.43	0.57
Mean NO_3^- concentration (mg N L^{-1})	0.38	0.55	0.41	1.16
CV of TN concentration (Unitless)	0.25	0.23	0.30	0.38
CV of NH_4^+ concentration (Unitless)	0.92	1.25	0.85	0.93
CV of NO_3^- concentration (Unitless)	0.83	0.58	0.40	0.47

Agricultural land includes paddy field, garden plot and upland; developed land includes residential, roads, mining and industrial lands; barren land includes water surface, wetlands, rock and natural reservation lands; domestic livestock includes pigs, rabbits, cows and sheep; poultry includes chickens and ducks. All values are the average for each time period. CV is short for the coefficient of variation.

30 ton day^{-1}. Since 2000, the watershed experienced a ~ 49% reduction in N fertilizer application and a ~ 73% decrease in the domestic animal population (on an equivalent number of pigs basis) (Fig. 2).

2.2. *Data sources*

2.2.1. *Water quality and hydrometeorological data*

River water samples were collected once every 4–8 weeks (n = 366) at Baizhiao station (watershed outlet, Fig. 1) during the 1980–2019 study period, with bimonthly sampling campaigns mainly during the 1995–1998 and 2003–2012 periods. Total nitrogen (TN), nitrate (NO_3^-) and ammonia (NH_4^+) concentrations for the 1980–2012 period were provided by the Taizhou City Environment Protection Bureau and monthly data for the October 2014–September 2019 period were collected/analyzed by our team. A groundwater monitoring well was

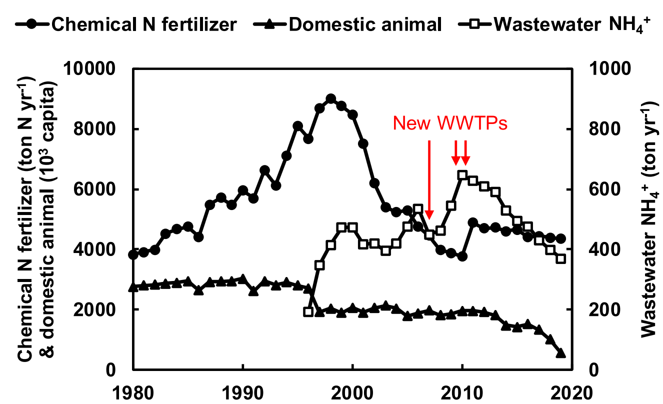

Fig. 2. Historical trends for chemical N fertilizer application, domestic animal populations (as pig equivalents based on N excretion), and total NH + 4 load from industrial and municipal wastewater discharge in the Yongan River watershed over the 1980–2019 period. Red arrows represent implementation of new wastewater treatment plants (one in 2007 and two in 2010). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

established (15 m depth, Fig. 1) near Baizhiao station and groundwater NO_3^- concentrations were measured monthly for the period of 2014–2019 (n = 62). Mixed river samples (three samples across the river cross section) and groundwater samples were collected between 8:00 a.m. and 9:00 a.m. on each sampling date, acidified with H_2SO_4 in the field (10 ml of concentrated H_2SO_4 per liter) and analyzed within 4 h of sampling. Nitrate concentration was determined by the spectrophotometric phenol disulfonic acid method (limit of detection: LOD = 0.01 mg N L^{-1}); NH_4^+ by the spectrophotometric salicylic acid method (LOD = 0.02 mg N L^{-1}); TN by persulfate digestion with UV spectrophotometric detection of NO_3^- (LOD = 0.04 mg N L^{-1}), respectively (State Environmental Protection Administration of China, 2002). Daily river discharge and precipitation amounts at three weather monitoring stations within the watershed for the 1980–2019 period were obtained from the local Hydrology Bureau and Weather Bureau, respectively.

2.2.2. *Anthropogenic nitrogen input data*

Annual livestock and poultry quantities, fertilizer application, land-use types and population data for the 1980–2019 period, as well as the NH_4^+ load from municipal sewage and industrial wastewater in the 1996–2019 period (Fig. 2, Table 1) were derived from local yearbooks of Xianju County and Linhai City. To address long-term changes in livestock populations, the number of each domestic animal type was converted into an equivalent number of pigs (Fig. 2) based on their N excretion rates (Han et al., 2014).

2.3. Weighted Regressions on Time, discharge and season (WRTDS) model calibration

This study adopted the WRTDS model to estimate daily riverine N concentration and loads from the discrete water quality measurements in the Yongan River during 1980–2019. The basic regression equation of WRTDS is expressed as (Hirsch et al., 2010):

$$ln(c) = \beta_0 + \beta_1 t + \beta_2 ln(Q) + \beta_3 sin(2\pi t) + \beta_4 cos(2\pi t) + \varepsilon \quad (1)$$

where ln is natural log, c is riverine N concentration (mg N L^{-1}), t is the time in decimal year, Q is measured daily average water discharge ($m^3\ s^{-1}$), $\beta_0 \sim \beta_4$ are fitted coefficients, and ε is the unexplained variation. The coefficients $\beta_0 \sim \beta_4$ and ε are allowed to vary in a gradual manner throughout the river water discharge and time regimes. The WRTDS model and its analysis procedures were available as the EGRET package (Version 3.0.2) in the R computing framework, which were fully described in Hirsch and De Cicco (2015)

According to the data requirements for the WRTDS model (Hirsch et al., 2010), the long-term data series (40 years) from the Yongan River having a large number of data points (n = 366) and daily river water discharge meets the necessary requirements. The metrics of coefficient of determination (R^2) and bias (Hirsch, 2014; Hirsch and De Cicco, 2015) were adopted to assess the performance of the WRTDS model calibration. WRTDS model uses a window approach to give each sampling point a corresponding weight based on the product of weighted values in the three dimensions of time, season and ln(Q). The weights were expressed as a function of the "distance" between the estimation point and the sample points, which is measured by the window parameters ($window_Y$, $window_S$ and $window_Q$). Our previous modeling results for the Yongan River watershed indicated that there was a ~ 7–13 year lag time between agricultural anthropogenic N inputs and riverine N export, whereas there was a negligible lag time between wastewater N discharge and riverine N export (Chen et al., 2014; Hu et al., 2018). Therefore, the parameter $window_Y$ was set from 5 years [the minimum value of $window_Y$ contained 100 observations with nonzero weights (Hirsch et al., 2010)] to 15 years to determine the optimal $window_Y$ values for simulating river TN, NH_4^+ and NO_3^- concentrations based on the model performances (R^2 and bias values). Other parameters of the model were set at default values (e.g., 0.5 years for $window_S$ and 2 natural log units for $window_Q$) in this study.

Using the calibrated WRTDS model, we obtained comprehensive predictions for TN, NO_3^- and NH_4^+ throughout the discharge and time regimes. The flow-normalized N concentrations/loads were estimated as the average of the estimated concentration under the full set of discharge conditions occurring on a given calendar date, thereby eliminating the influence of random temporal variability in streamflow when assessing the impacts of relevant anthropogenic interventions. The uncertainty analysis was conducted with the WRTDS Bootstrap Test (wBT) procedure using the EGRETci R package (Version 2.0.3) to quantify 90% confidence intervals (CI) and likelihoods of riverine N trends (Hirsch et al., 2015). Using the FN_{2Q} approach provided by Zhang et al. (2021), riverine flow-normalized NH_4^+ concentrations and loads were further decomposed into different hydrological conditions (i.e., high and low flows regimes) to address potential influencing factors on riverine NH_4^+ dynamics. High and low flows regimes represented the upper 50% and the lower 50% of the discharge records, respectively. To address potential contributions from groundwater and soil N pools, annual average riverine NO_3^- concentrations following conditions of "10-day of no-precipitation" and "first rainstorm event (>30 mm per 24 hr) after a 10-day no-precipitation period" were estimated for each year by the calibrated WRTDS model. All correlation and regression analyses (e.g. R^2 and coefficient of variation (CV)) were performed using functions in the R computing framework (R Development Core Team, 2012).

3. Results and discussion

3.1. Performance of the WRTDS model

Overall, the model performances (R^2 and bias values) for simulating river TN and NO_3^- concentrations were relatively stable when $window_Y$ values varied between 5 and 15 years (Fig. 3). Model performances for NH_4^+ were also stable when the $window_Y$ values ranged from 5 to 10 years, whereas performance decreased significantly when the $window_Y$ value was>10 years. These results indicated that the WRTDS model performances were not sensitive to $window_Y$ values (Hirsch et al., 2010). According to the previously identified lag times (~7–13 yr) between anthropogenic N inputs and riverine N exports in the Yongan River watershed (Chen et al., 2014; Hu et al., 2018) and the recommended model default values (Hirsch et al., 2010), we selected 13, 13 and 5 years as the $window_Y$ values for TN, NO_3^- and NH_4^+ simulations, respectively.

The calibrated WRTDS model provided reasonable results for predicting riverine N concentrations and loads in the Yongan River (Fig. 4). The modeled riverine TN, NH_4^+ and NO_3^- concentrations, as well as loads, presented good agreement with observed values ($R^2 > 0.55$). The R^2 values between modeled and observed TN, NH_4^+ and NO_3^- concentrations or loads fell within the range of estimated R^2 values (~0.05–0.85 for concentrations and ~ 0.60–0.97 for loads) in previous applications of the WRTDS model (Oelsner et al., 2017). Bias values between observed and modeled TN, NH_4^+ and NO_3^- loads were 0.013, −0.048 and 0.040, respectively, which fell within the acceptable bias range of −0.1–0.1 for the WRTDS model (Hirsch, 2014; Hirsch and De

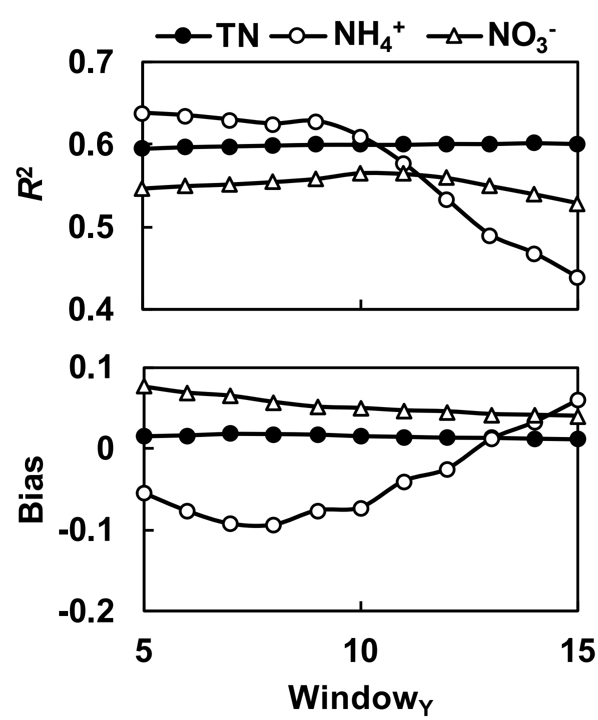

Fig. 3. WRTDS model performances (R^2 for concentration and bias values) for simulating riverine TN, NO_3^- and NH_4^+ concentrations under different values for the parameter $window_Y$ in the Yongan River over the 1980–2019 period.

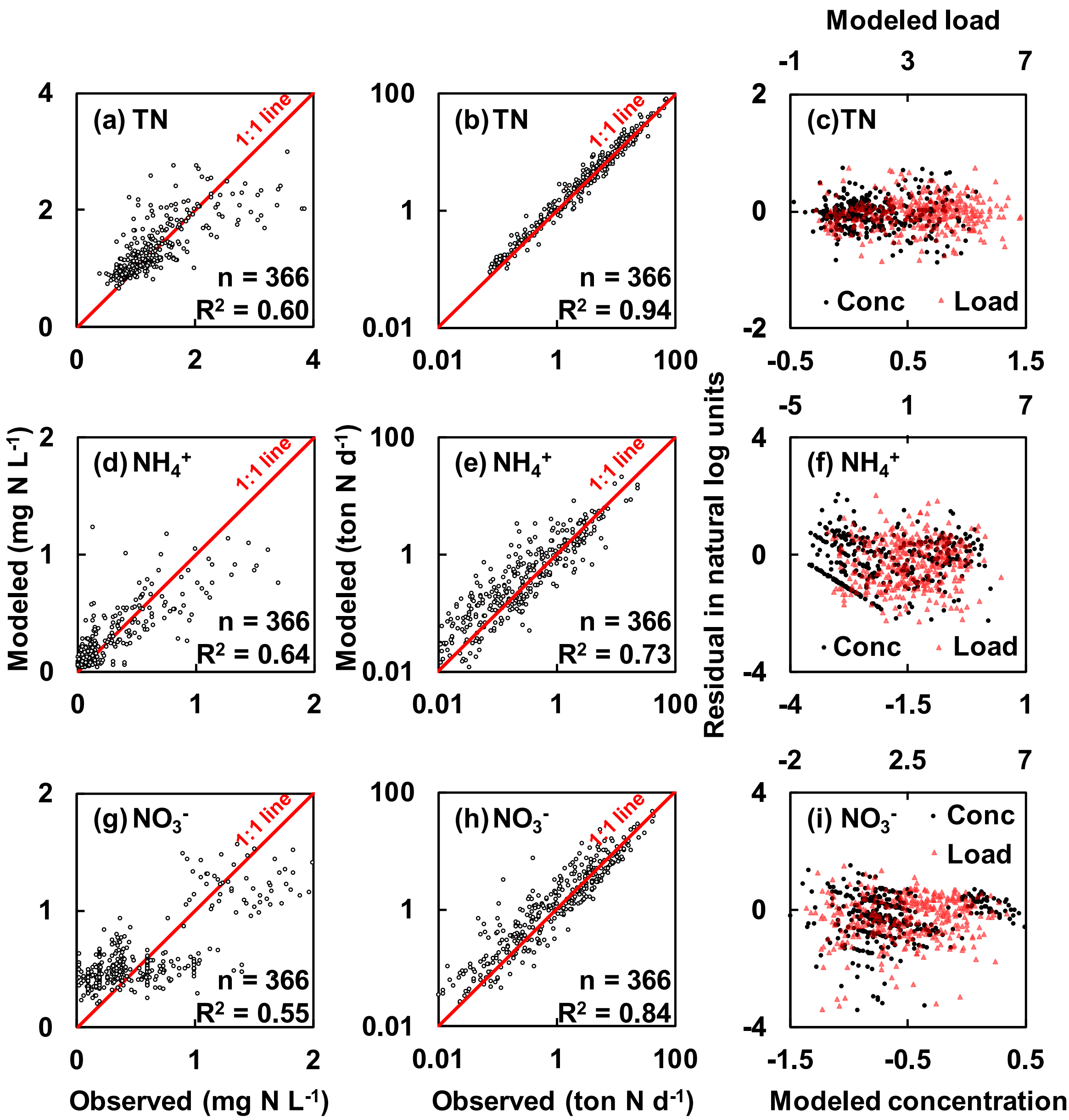

Fig. 4. Model results for daily concentrations of (a) TN, (d) NH + 4and (g) NO− 3 and daily loads of (b) TN, (e) NH + 4 and (h) NO− 3 showing observed versus modeled values, and plots for (c) TN, (f) NH + 4 and (i) NO− 3 model residuals (in natural log units) versus concentration (black dots) and load (red triangles) values (in natural log units) using the WRTDS model in the Yongan River from 1980 to 2019. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Cicco, 2015). Determined load bias values in this study were comparable to previous applications of the WRTDS model in other river systems: −0.044–0.031 for nitrate in the Mississippi River (Sprague et al., 2011), −0.002 for nitrate in the Raccoon River (Hirsch, 2014), ~0.003 for TN/NO_x in the Chesapeake Bay watershed (Zhang et al., 2019) and −0.087–0.083 for TN/NO_x concentrations and loads in 471 stream sites across the United States (Oelsner et al., 2017). This pattern indicates that the estimated concentrations and loads were consistent with the observed pattern. These results confirm that the calibrated WRTDS model was effective for estimating daily concentrations and loads for TN, NH_4^+ and NO_3^- in the Yongan River over the 1980–2019 period.

The model performances for N load (product of concentration and discharge) simulations were better than those of N concentrations (Fig. 4), which is attributed to the higher temporal variability in river discharge than N concentrations (Table 1). The temporal variability of riverine N loads was also more dependent on water discharge (R^2 = 0.50–0.86) than concentrations (R^2 = 0.001–0.03). Moreover, since concentrations were simulated by the WRTDS model while discharges were from monitored results, performances for modeled loads were generally better than those of concentrations (Fig. 4). The residuals of model results were independent of mean N concentrations or loads with a symmetry around the zero line (Fig. 4c, f, i, $p > 0.05$) and no significant differences with respect to discharge, time, or seasonal components (Fig. 5), indicating robust model results. Higher residuals were observed in 1980–2000, which could be attributed to relative higher variability of N concentrations (especially for NH_4^+ and NO_3^-, Table 1) and lower sampling frequency (6 times per year) in some years. Therefore, it is warranted to increase N monitoring frequency and/or adding storm sampling to improve accuracy in future applications of the WRTDS model (Oelsner et al., 2017).

3.2. *Long-term change of riverine NH_4^+ level*

In the Yongan River watershed, the WRTDS model estimated that

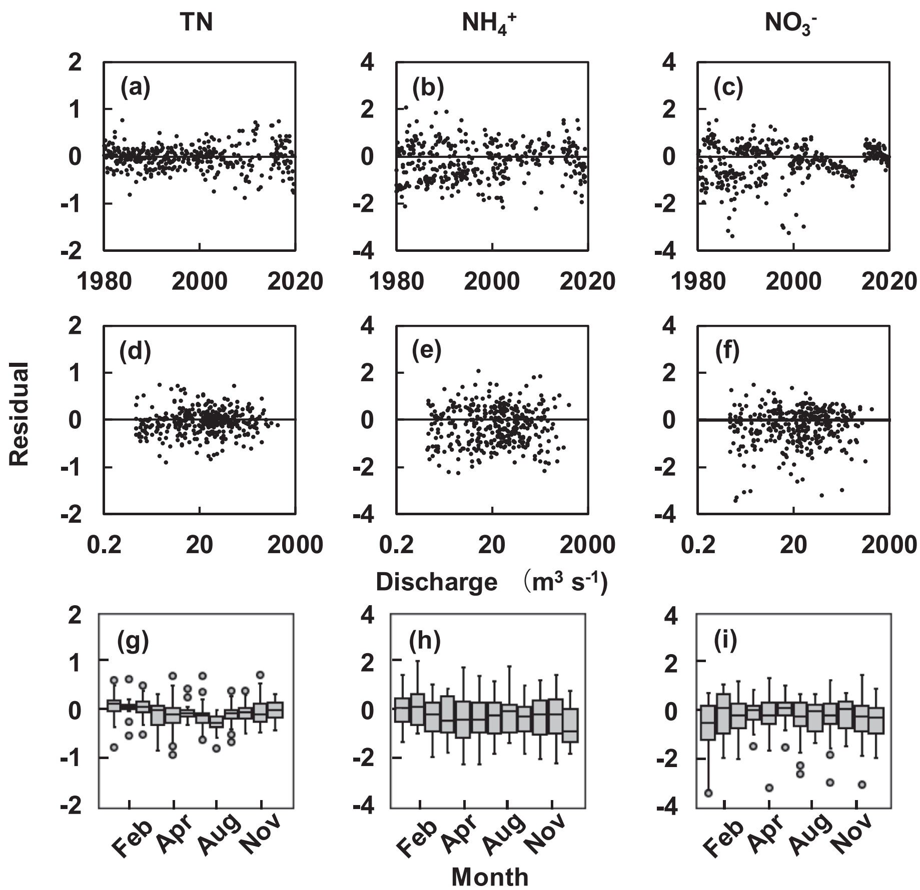

Fig. 5. WRTDS modeled residuals for riverine TN, NH + 4 and NO– 3 concentrations versus time (a-c), river discharge (d-f), and month (g-i) for the Yongan River in 1980–2019.

annual riverine flow-normalized NH_4^+ concentration increased from 0.09 (90% CI: 0.06–0.12) mg N L^{-1} in 1980 to a peak of 0.80 (0.71–0.99) mg N L^{-1} in 2009 before progressively declining to 0.30 (0.13–0.42) mg N L^{-1} in 2019 (Fig. 6). In 2005–2015, annul average NH_4^+ concentration exceeded the category III standard for Chinese surface waters (0.5 mg N L^{-1}, GB3838-2002). Correspondingly, the estimated annual riverine flow-normalized NH_4^+ load rapidly increased from 2.76 × 10^5 (1.58–4.04 × 10^5) kg N yr^{-1} in 1980 to reach a peak of 14.45 × 10^5 (9.82–18.77 × 10^5) kg N yr^{-1} in 2008 and then decreased to 6.50 × 10^5 (3.27–8.82 × 10^5) kg N yr^{-1} in 2019. The proportion of riverine TN comprised of NH_4^+ increased from 10% in 1980 to 47% in 2009 before declining to 12% in 2019 (Fig. 6). Estimated likelihood values (0.99) for flow-normalized NH_4^+ concentrations/loads showed "highly likely" increasing trends in the 1980–2009 period and "highly likely" decreasing trends in the 2009–2019 period (Fig. 6, Hirsch et al., 2015).

In general, NH_4^+ is readily adsorbed to soil and river bed substrates by cation exchange reactions (Craig et al., 2008) and/or converted to nitrate by soil/in-stream nitrification (Hu et al., 2019) resulting in low NH_4^+ concentrations in most natural waters. Therefore, anthropogenic point source pollution (i.e., domestic and industrial wastewater discharges) is the dominant source of elevated riverine NH_4^+ levels in most cases (Huang et al., 2014). This inference is supported by the dilution pattern observed between riverine NH_4^+ concentration and water discharge (i.e., lower and higher concentrations occurred in high and low flow regimes, respectively, Fig. 7b and Fig. 8a). Additionally, the flow-normalized NH_4^+ load during the low-flow regime ($R^2 = 0.62$, $p < 0.01$) was more dependent on wastewater NH_4^+ discharge load than that during the high-flow regime ($R^2 = 0.46$, $p < 0.01$). Therefore, the mitigation of riverine NH_4^+ pollution in the Yongan River watershed was mainly ascribed to improvements in wastewater collection/treatment along with some reductions in animal waste runoff owing to reductions in livestock populations.

The rapid increase in riverine NH_4^+ levels during the 1980–2009 period (Fig. 6) were attributed to increasing industrial and domestic wastewater discharged directly into the river network in the absence of wastewater treatment plants (WWTPs) (Jin et al., 2014). This period of time corresponds to rapid urbanization and industrial development, as well as a rapidly increasing population density in the Yongan River watershed (Table 1). Consequently, annual wastewater NH_4^+ discharge increased by 233% between 1996 and 2010 (Fig. 2). Notably, the riverine NH_4^+ load increased following the establishment of the first new WWTP in 2007. We ascribe this increased NH_4^+ load to the continuous increase of local wastewater amounts due to rapidly growing population and industries during this time period, thereby limiting the observed impacts of the first new WWTP. Conversely, the large decline in riverine NH_4^+ levels during the 2010–2019 period were mainly associated with the 43% decrease in wastewater NH_4^+ discharge load between 2010 and 2019 (Fig. 2) due to construction of three new central WWTPs in urban areas, as well as enhanced industrial wastewater treatment and improved rural domestic sewage treatment. Quantitatively, the decrease of urban domestic wastewater NH_4^+ discharge corresponds to a reduction in annual average riverine NH_4^+ concentration by ~ 0.1 mg N L^{-1} (20%). It is difficult to estimate the contribution of enhanced rural domestic wastewater treatment and individual industrial enterprise wastewater treatment to riverine NH_4^+ concentration. However, the greater decline in NH_4^+ concentrations in autumn/winter (~74%) than in spring/summer (~58%) during 2010–2019 (Fig. 7b, Fig. 7e) supports the importance of wastewater treatment, since point source pollution is most strongly expressed in the dormant/dry season, which is also the low flow regime (i.e., less

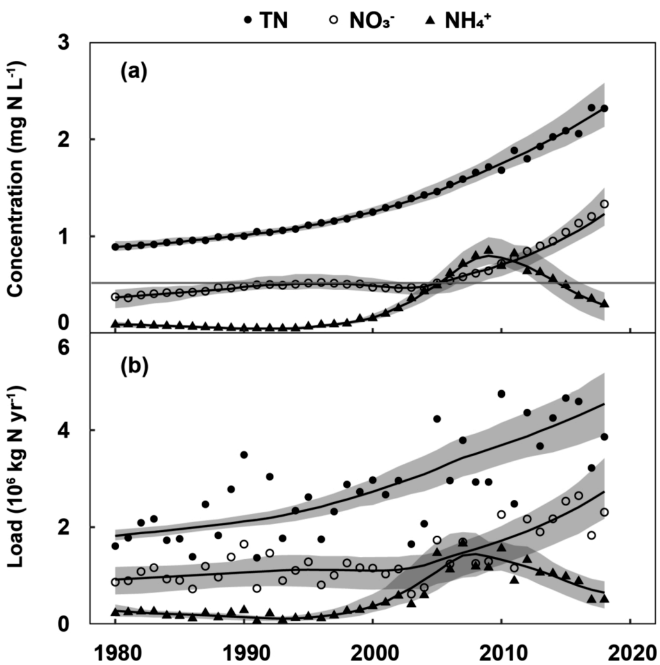

Fig. 6. Historical trends for riverine (a) annual mean estimated (dots) and flow-normalized (line) concentrations, and (b) annual total estimated (dots) and flow-normalized (line) loads of TN, NO– 3 and NH + 4 in the Yongan River from 1980 to 2019. The red horizontal line in (a) represents the NH + 4 concentration criteria (0.5 mg N L^{-1}) for Chinese category III water (GB3838-2002). Shaded area denotes 90% confidence intervals for annual average riverine flow-normalized concentrations and loads. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

dilution) in this watershed (Hu et al., 2018). Overall, these results indicate that mitigation of NH_4^+ pollution in the Yongan River was strongly improved by implementation of greater wastewater treatment capacity/efficiency to reduce point source pollution.

3.3. Long-term changes of riverine TN and NO_3^- levels

For the Yongan River, the WRTDS model estimated that annual flow-normalized TN concentration continuously increased from 0.89 (90% CI: 0.85–0.95) mg N L^{-1} in 1980 to 2.32 (2.13–2.58) mg N L^{-1} in 2019, resulting in a 161% increase (~74% increase in 2000 s). The increased TN concentrations resulted in a related increase in the annual flow-normalized TN load from 1.82 × 10^6 kg (1.73–1.95 × 10^6) N yr^{-1} to 4.54 × 10^6 (3.89–5.17 × 10^6) kg N yr^{-1} (Fig. 6). Moreover, annual flow-normalized NO_3^- concentration increased by 232% over the 40-yr study period (Fig. 6), with a steady increased from 0.37 (0.26–0.45) mg N L^{-1} in 1980 to 1.23 (1.11–1.50) mg N L^{-1} in 2019 (~86% increase in 2000 s). This resulted in a corresponding increase in the annual flow-normalized NO_3^- load from 0.90 × 10^6 (0.62–1.18 × 10^6) kg N yr^{-1} in 1980 to 2.73 × 10^6 (2.17–3.42 × 10^6) kg N yr^{-1} in 2019. Estimated likelihood values (0.99) for flow-normalized TN and NO_3^- concentrations/loads showed "highly likely" increasing trends during the study period (Fig. 6, Hirsch et al., 2015). The ratio of riverine NO_3^- to TN fluctuated within a narrow range of 45% to 50%, with a trend for higher proportions since 2012–2019.

Nitrate is the predominant form of N in many agricultural watersheds because it is highly mobile and readily leached from soils (Craig et al., 2008), resulting in high riverine NO_3^- concentrations usually occurring in high flow regimes (Fig. 7c). Due to lack of data concerning wastewater NO_3^- and TN loads, it was not possible to evaluate the impacts of WWTP facilities on riverine NO_3^- and TN concentrations. However, the impacts of WWTPs on NO_3^- and TN appeared to be limited as indicated by continuous increasing trends in observed riverine NO_3^- and TN concentrations between 2007 and 2019. Previous dual stable isotope (^{15}N-NO_3^-/^{18}O-NO_3^-) analysis for the Yongan River in 2014–2017 indicated that wastewater contributed to 25 ± 15% of the riverine NO_3^- load (Hu et al., 2019). Therefore, nonpoint source pollution is inferred to be the dominant contribution of riverine NO_3^-/TN in the Yongan River watershed. In contrast to the increasing concentrations of riverine NO_3^-/TN, annual chemical N fertilizer application decreased by 49% in 2000–2019 and domestic livestock numbers decreased by 73% since 1980 (Fig. 2). Such contrasting trends between watershed N source inputs and riverine NO_3^-/TN levels are attributed to contributions of legacy N accumulated in soils and groundwater, that have a purported lag time of 7–13 years in the Yongan River watershed (Chen et al., 2014; Huang et al., 2014; Hu et al., 2018).

The WRTDS model estimated annual average riverine NO_3^- concentration for the 10-day no-precipitation condition increased 3.8-fold between 1980 and 2019 (86% increase observed in 2000–2019, Fig. 9a) in the Yongan River watershed. This implies an increasing contribution of groundwater N to riverine N loads during stable base-flow conditions (Chen et al., 2014; Hu et al., 2018; Van Meter et al., 2016). This is supported by an increasing NO_3^- concentration in groundwater near the outlet of the watershed during the 2014–2019 period (Fig. 9b). Furthermore, the annual average NO_3^- concentration for the first rainstorm events after 10-days with no-precipitation (associated with soil profile flushing) increased 4.1-fold in the 1980–2019 period (91% increase in 2000–2019, Fig. 9a). The average riverine NO_3^- concentration for the first rainstorm event after 10-day with no-precipitation (0.99 mg N L^{-1}) was ~ 18% higher than that observed for the 10-day no-precipitation condition (0.83 mg N L^{-1}) during the past 10 years. These results are attributed to an increasing N contribution from soil organic N mineralization to riverine N pollution in recent years. Dry antecedent conditions allow accumulation of mineral N from soil organic N mineralization, that is subsequently leached from the soil profile to surface waters during rainstorm events (Kopáček et al., 2013; Xiang et al., 2008). Previous modeling and dual isotope (^{2}H-H_2O /^{18}O-H_2O) studies in the Yongan River watershed indicated that slow subsurface flow and groundwater contributed > 75% of annual river discharge with a mean transit time of 4.5 yr, and contributed 58–81% of the riverine TN load through groundwater transport (Hu et al., 2018; Hu et al., 2019; Hu et al., 2020).

Our dual stable isotope (^{15}N-NO_3^-/^{18}O-NO_3^-) analysis for the Yongan River from 2014 to 2017 further demonstrated that soil and groundwater sources contributed 33 ± 8% and 43 ± 17% of riverine NO_3^- loads, respectively (Hu et al., 2019). A previous modeling study similarly predicted that soil organic N mineralization and release contributed 35%, on average, to riverine TN export load in the Yongan River watershed during the 1980–2009 period (Chen et al., 2014). Increasing contributions of soil and groundwater legacy N pools to riverine NO_3^- loads are also supported by decreasing coefficients of variance for monthly NO_3^- concentrations in the 2000–2019 period ($p < 0.01$). Additionally, there was no significant seasonal variation in the rate of increase for NO_3^- concentrations during this period (Fig. 7f). Collectively, these data/modeling results suggest that soil and groundwater legacy N sources mask any response of riverine NO_3^-/TN concentrations to nonpoint source pollution control measures in the Yongan River watershed.

3.4. Implications for riverine N pollution control

For the Yongan River watershed, the WRTDS model confirmed the efficacy of point source pollution control efforts as demonstrated by decreased riverine NH_4^+ levels resulting from improvements in urban, industrial and rural wastewater treatment. Conversely, the model did not detect improvements in nonpoint source pollution control as riverine NO_3^- and TN levels continued to increase over the study period. Despite the appreciable reductions in NH_4^+ point source inputs, riverine

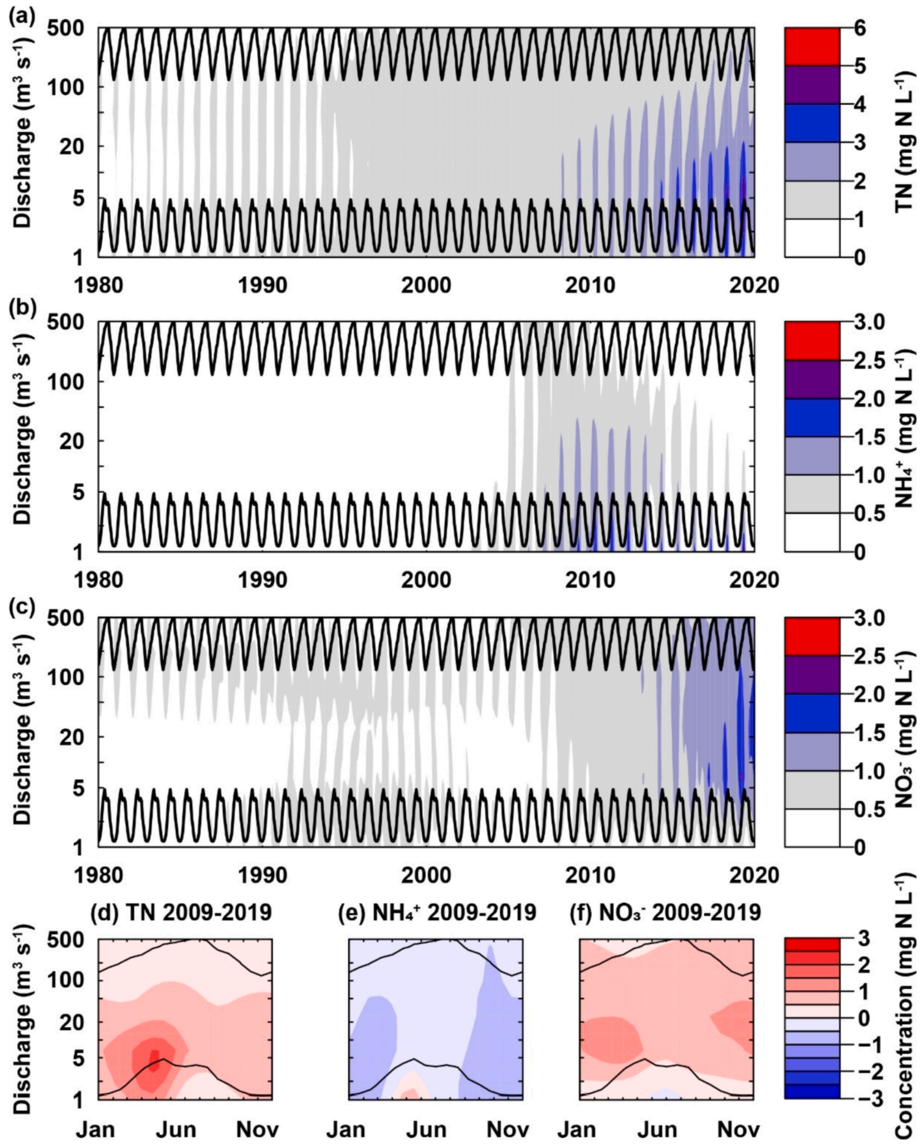

Fig. 7. Contour plots displaying a colored gradient for estimated (a) TN, (b) NO– 3 and (b) NH + 4 concentrations in 1980–2019 and seasonal changes for (d) TN, (e) NO– 3 and (f) NH + 4 concentrations in 2009–2019 in the Yongan River. The black line on the plot represents the 95th percentile of daily discharge. Estimated concentrations were generated using the WRTDS model.

NH_4^+ concentration was not able to meet category III -V water quality standards (Chinese national criteria) during the low-mid discharge regimes in spring when dilution capacity was low (Fig. 7b). High NH_4^+ concentrations in surface waters pose appreciably risks to downstream aquatic ecosystems, such as ammonia toxicity, eutrophication and hypoxia resulting from oxygen consumption during nitrification (Camargo and Alonso, 2006). Therefore, wastewater collection and treatment should be further enhanced with a particular focus on rural areas where wastewater collection/treatment is not fully implemented. Decreased recycling of human and animal excreta as an agricultural nutrient source over the past several decades (Gu et al., 2015) and the lack of efficient sewage collection/treatment in rural areas (Chen et al., 2013) are major causes of increased NH_4^+ pollution in many regions in China and throughout the developing world. Increased recycling of human and domestic animal wastes would partially replace chemical fertilizer use on croplands while simultaneously reducing wastewater discharge to river systems (Strokal et al., 2016).

Remediation strategies to decrease riverine NO_3^- and TN pollution must focus on further reductions in nonpoint source pollution sources and recognize the importance of legacy N sources. Results of this study in combination with our previous studies (Chen et al., 2014; Hu et al., 2018; Hu et al., 2019) confirm the large contribution of nonpoint source pollution derived from legacy N pools originating from soil and groundwater (Fig. 9). Legacy N pools accumulated in soil and groundwater from historical applications of excess N are slowly working their way through the soil and groundwater systems to serve as a long-term source of riverine N in the Yongan River watershed (Fig. 9). Legacy N sources are now well known as a considerable long-term source of riverine N in many watersheds worldwide (Chen et al., 2018; Van Meter et al., 2016; Van Meter and Basu, 2017). Thus, in addition to N source controls, it is warranted to adopt N-interception measures along the hydrologic flowpath, such as using flow-through wetlands, riparian buffer strips, step pools or other physical modifications to reduce N loading to rivers (Chen et al., 2011; Craig et al., 2008). Utilization of legacy soil N reserves should be considered as a nutrient source for crop production by utilizing soil organic N mineralization as a source of N for crop requirements and/or agroforestry practices to extract, sequester and recycle deeper soil N sources (Chen et al., 2018). To coped with catchment-scale legacy groundwater N pollution, restoration of stream and riparian zones is a compelling strategy for enhancing groundwater

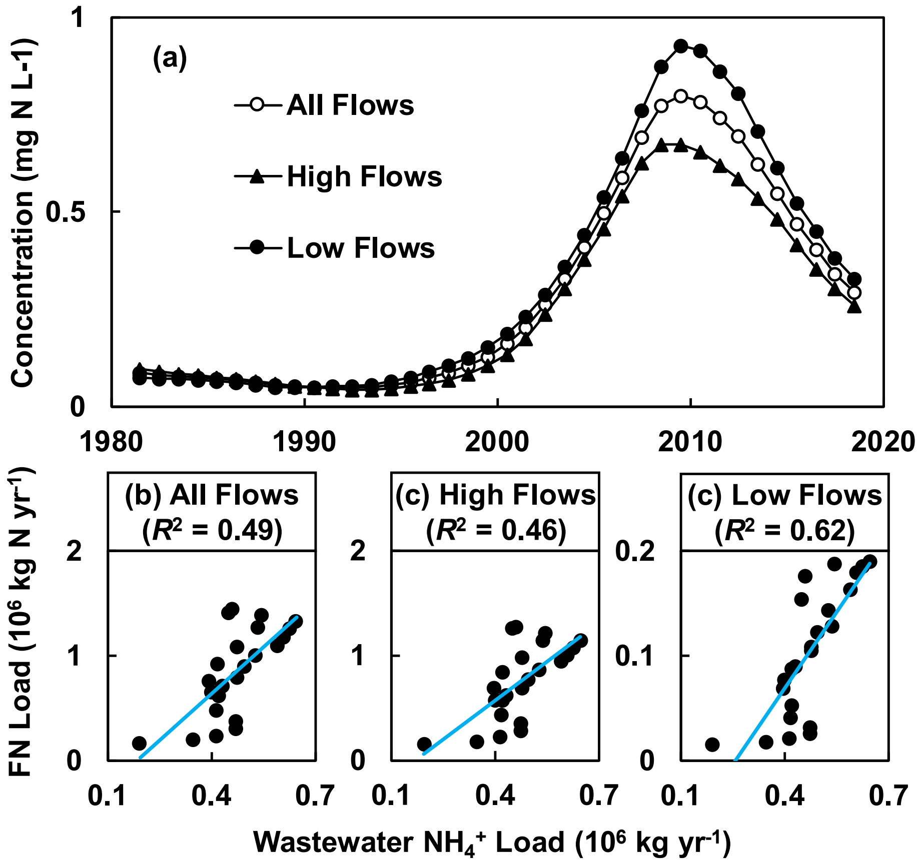

Fig. 8. Estimated (a) annual NH + 4 flow-normalized (FN) concentration under all flows, high flows (upper 50%) and low flows (lower 50% of discharge records) regimes in 1980–2019, and correlations between watershed wastewater NH + 4 load and annual flow-normalized NH + 4 load under (b) all flow, (c) high flow, and (d) low flow regimes in 1996–2019 for the Yongan River watershed.

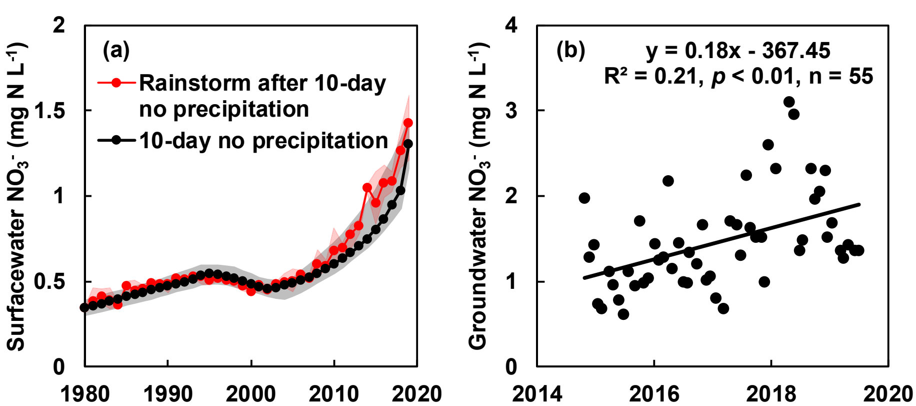

Fig. 9. (a) Average riverine NO– 3 concentrations for antecedent conditions of "10-days with no precipitation" and the "first stormflow after 10-days with no-precipitation" in 1980–2019 for the Yongan River watershed. Shadow area denotes 95% confidence interval for NO– 3 concentrations after rainstorm (red) and after 10-day dry period (gray). (b) Trend for groundwater NO– 3 concentrations (line is linear regression) at the outlet of Yongan River watershed from December 2014 to August 2019. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

NO_3^- removal by denitrification (Boano et al., 2014). Permeable reactive barrier technology also provides a promising approach for sustainable *in situ* groundwater restoration that makes use of natural groundwater flows to transport NO_3^--rich groundwater to reactive materials for NO_3^- removal by microbial denitrification (Liu et al., 2013; Obiri-Nyarko et al., 2014).

4. Conclusion

Herein, we demonstrated the efficacy of the WRTDS model for evaluating changes in long-term riverine N dynamics in response to implementation of pollution control measures in a nitrogen-rich river network of eastern China. The WRTDS model showed satisfactory accuracies for predicting daily riverine total N, NH_4^+ and NO_3^- concentrations/loads across the 40-year study period (1980–2019). Modeled results indicated that riverine NH_4^+ concentration rapidly increased in 1980–2009, and then decreased in 2010–2019 owing to decreased wastewater NH_4^+ loads (2010–2019) from improved wastewater collection/treatment. Although chemical N fertilizer use and domestic animal numbers both decreased in 2000–2019, riverine TN and NO_3^- concentrations continued to increase during the 1980–2019 period. This paradox is ascribed to contributions of legacy N from soil and groundwater sources. Therefore, point source pollution control efforts demonstrated improved effectiveness, whereas nonpoint source pollution control requires additional efforts, especially to address legacy N pollution issues. The WRTDS model provides a useful tool for identifying long-term riverine N pollution trends and sources, providing decision-makers with critical information for developing/optimizing watershed N pollution control strategies.

CRediT authorship contribution statement

Kaibin Wu: Data curation, Methodology, Software, Validation. **Minpeng Hu:** Methodology, Investigation, Data curation. **Yufu Zhang:** Methodology, Software, Validation. **Jia Zhou:** Investigation, Data curation. **Hao Wu:** Investigation, Data curation. **Mingfeng Wang:** Investigation, Data curation. **Dingjiang Chen:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – review & editing, Supervision.

Declaration of Competing Interest

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

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