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Influence of Lag Effect, Soil Release, And Climate Change on Watershed Anthropogenic Nitrogen Inputs and Riverine Export Dynamics

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Ⓢ Supporting Information

ABSTRACT: This study demonstrates the importance of the nitrogen-leaching lag effect, soil nitrogen release, and climate change on anthropogenic N inputs (NANI) and riverine total nitrogen (TN) export dynamics using a 30-yr record for the Yongan River watershed in eastern China. Cross-correlation analysis indicated a 7-yr, 5-yr, and 4-yr lag time in riverine TN export in response to changes in NANI, temperature, and drained agricultural land area, respectively. Enhanced by warmer temperature and improved agricultural drainage, the upper 20 cm of agricultural soils released 270 kg N ha^{-1} between 1980 and 2009. Climate change also increased the fractional export of NANI to river. An empirical model (R^2 = 0.96) for annual riverine TN flux incorporating these influencing factors estimated 35%, 41%, and 24% of riverine TN flux originated from the soil N pool, NANI, and background N sources, respectively. The model forecasted an increase of 45%, 25%, and 6% and a decrease of 13% in riverine TN flux from 2010 to 2030 under continued development, climate change, status-quo, and tackling scenarios, respectively. The lag effect, soil N release, and climate change delay riverine TN export reductions with respect to decreases in NANI and should be considered in developing and evaluating N management measures.
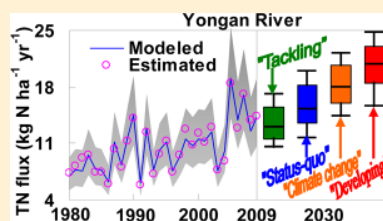
INTRODUCTION

Human activities have approximately doubled the reactive nitrogen (N) on Earth,[1] often resulting in elevated N fluxes in rivers.[2−5] A quantitative understanding of the dynamic relationship between anthropogenic N inputs and riverine N flux is required for developing efficient watershed N pollution control measures.[2−4] Net anthropogenic nitrogen input (NANI) is a nitrogen-budgeting approach that sums N contributions from atmospheric deposition, fertilizer application, agricultural N fixation, and net N import/export in feed, food, and seed to a watershed.[6−9] NANI has been widely recognized as an effective tool to explain among-watershed or among-year variations in riverine N fluxes.[2−4,10,11] However, the NANI budgeting approach as well as lumped watershed models such as export coefficient models, SPARROW, and PolFlow[12−15] generally assume that the N status of soil, aquifers, and biomass is at steady state (at least over a multiyear period).[10,11] Therefore, these models do not rigorously address the N-leaching lag time defined as the time elapsed between
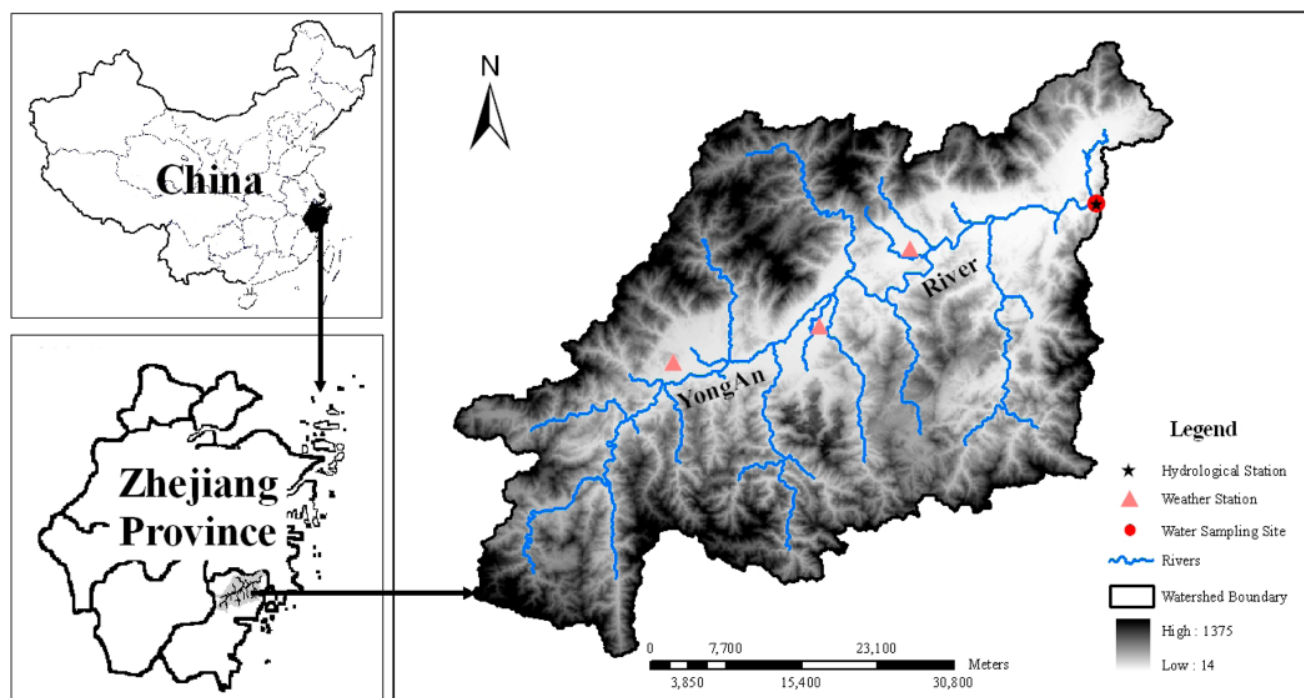
Figure 1. Location of the Yongan River watershed in China and Zhejiang Province and the water quality sampling site and weather stations.

changes in human activities (e.g., N input) and climate change (e.g., increasing temperature) and the resulting changes in riverine N export at the watershed scale.[15−19] N-leaching lag times mainly result from the long transit time of N passing through soil and vadose/groundwater zones to rivers[15−19] and are regulated by integrated hydrological and biogeochemical processes.[16,19] Lag times have been reported to range from several months to several decades.[19,20] Although the NANI budgeting approach and lumped watershed models are commonly applied using a multiyear average temporal resolution to reduce the uncertainty derived from the lag time, a major challenge remains in determining the appropriate length of the multiyear period that should be used to estimate average N inputs to satisfy the steady-state assumption for predicting riverine N export.

The soil is a key interface linking anthropogenic N inputs to river N exports within a watershed. Soil may alternate as a sink or source in regulating the fraction of NANI exported by rivers.[7,21,22] In addition to NANI, net soil organic N mineralization (i.e., difference between mineralization and immobilization) has a considerable potential to export N to rivers.[2,8,19] In some studies, a large part (25−80%) of the exported N may originate from the mineralization of soil organic N rather than from applied fertilizers or manures.[7,22,24] Soil organic N mineralization is highly dependent on soil aeration, moisture, and temperature;[25,26] thus it can be enhanced by tillage and artificial drainage[7,27] as well as by climate warming[26,28] and hydroclimate change.[22,29,30] From the perspective of climate change and increasing soil disturbance, net soil N mineralization will be enhanced and subsequently has the potential to contribute to a considerable riverine N flux. Due to the unavailability of extensive temporal records for soil properties, changes in soil N status and its consequent influence on riverine N export have been rarely considered in addressing the dynamic relationship between watershed NANI and riverine N flux.

Overall, when examining the quantitative relationship between NANI and riverine N export, several questions remain to be answered: How long is the lag time between changes in N inputs and riverine export? What is the role of changes in soil N pools on riverine N export? How does climate change influence riverine N export? Using an extensive data record for the Yongan River watershed in eastern China from 1980 to 2009, this study demonstrated the importance of the N input-output lag effect, soil N release, and climate change on NANI and riverine TN export dynamics. To address the questions above, this study (i) employs a cross-correlation analysis to determine the lag time between changes in human activities and climate and change in riverine TN export, (ii) addresses the change of soil N status and its regulating factors, (iii) develops an empirical model that considers the lag effect, soil N release, and climate change for linking NANI to riverine TN flux, (iv) identifies individual contributions from NANI, soil N pool, and background N sources to riverine TN flux, and (v) predicts future trends in riverine N export based on scenarios for future (2010−2030) changes in human activities and climate. This study provides a methodology for evaluating the N-leaching lag time between NANI and riverine export and improves our understanding for why riverine N exports commonly continue to increase even after a significant decline in anthropogenic N inputs.[15,17,31−33]

■ MATERIALS AND METHODS

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

nonregulated having no dams or transboundary water withdrawals. The climate is subtropical monsoon with an average annual temperature of 17.4 °C and average annual precipitation of 1400 mm. Rainfall mainly occurs in May–September with a typhoon season in July–September. Over the 1980–2009 period, this watershed experienced ∼1.7 °C increase in annual air temperature, ∼22 days decrease in the number of rainy days, ∼30% increase in the coefficient of variation for daily rainfall, and ∼1-fold increase in storm events (>50 mm per 24 h), with no significant trends in annual precipitation amount or average river discharge (Supporting Information (SI), Part I, Figure S1).

Agricultural land (including paddy field, garden plot, and dry land) averaged ∼12% of total watershed area in 1980–2009, with developed land (including rural and urban residential lands, roads, and mining and industry lands), woodland, and barren land contributing ∼3%, ∼67%, and ∼18%, respectively. The economic role of agriculture has been increasingly replaced by industry since the 1990s, resulting in a remarkable reduction (∼40%) in chemical N fertilizer application since 2000. The agricultural land area irrigated and drained with cement channels and pipes increased by ∼2-fold since 2000 (SI, Part III).

River Nitrogen, Hydroclimate, and Soil Data. River water samples were collected once every 4–8 weeks during the 1980–2009 study period. Data on river TN and nitrate concentrations, daily river discharge, and daily precipitation and temperature at three weather monitoring stations within the watershed were obtained from the local Environment Protection Bureau, Hydrology Bureau, and Weather Bureau, respectively. To estimate annual TN flux based on the discrete monitoring data, the LOADEST model[34] was applied for predicting daily TN concentration, resulting in high R^2 (R^2 = 0.72, n = 238, p < 0.001) and low average relative error (±5%) between the modeled and measured TN concentrations (SI, Part II). Extensive soil samples (one composite sample per 15 ha for plain regions and one composite sample per 25 ha for hilly regions) were collected from the top 20 cm layer of agricultural lands (paddy field, dry land, and garden plot) in the watershed by the local Agriculture Bureau in 1984 and 2009. Soil organic matter and total nitrogen contents for the upper 20 cm soil layer were measured at the same location in both years to evaluate changes between 1984 and 2009, resulting in temporally paired soil organic matter (n = 305) and total N (n = 415) contents (SI, Part III).

Net Anthropogenic Nitrogen Input Estimate and Uncertainty Analysis. Annual NANI from 1980 to 2009 was estimated as the sum of five major components:[35,36] atmospheric N deposition, commercial organic and synthetic fertilizer N applications, agricultural N fixation, and net food and feed N input, and seed N input, where the net food and feed N import was calculated as the sum of human N consumption and livestock N consumption, minus the sum of livestock N production and crop N production (SI, Part IV).

To gain insight into the uncertainty of NANI estimation, an uncertainty analysis was performed using Monte Carlo simulation (SI, Part IV). A normal probability distribution with a 30% coefficient of variation was assumed for each parameter used in NANI estimation.[37,38] A total of 10 000 Monte Carlo simulations were performed to obtain the mean and 95% confidence interval for annual NANI values.

Cross-Correlation Test. Cross-correlation analysis is a standard statistical method to measure correlation between two

series of variables time-shifted against one another.[39] This approach was utilized to identify time lags between dependent (e.g., N export) and independent variables (e.g., NANI). The cross-correlation analysis was conducted using EViews software (version 6, Quantitative Micro Software Inc., 2002) (SI, Part V).

■ RESULTS AND DISCUSSION

Lag Effects of Human Activity and Climate Change on Riverine TN Export. Over the 30-yr record, annual average TN concentration in the Yongan River increased by 113% (Figure 2a) with a steady increase from 0.94 mg N L^{-1} in 1980
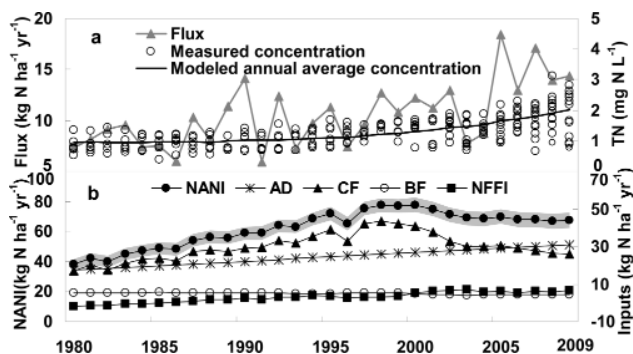
Figure 2. Historical trends for riverine TN flux, measured concentration, and LOADEST modeled annual average concentrations in the Yongan River watershed over the 1980–2009 period (a) and net anthropogenic N input (NANI) from atmospheric deposition (AD), chemical fertilizer (CF), biological fixation (BF), and net food, feed, seed input (NFFI) to watershed (b). Shadow area denotes 95% confidence interval of NANI derived from Monte Carlo simulation.

to 2.00 mg N L^{-1} in 2009 (26% increase in the 2000s). Annual riverine TN flux increased by 91% over the study period from an average 8.5 kg N ha^{-1} yr^{-1} in the 1980s, to 10.1 kg N ha^{-1} yr^{-1} in the 1990s, and 13.0 kg N ha^{-1} yr^{-1} in the 2000s (17% increase in the 2000s). Annual NANI rapidly increased from 38.0 kg N ha^{-1} yr^{-1} in 1980 to 76.9 kg N ha^{-1} yr^{-1} in 1999 (Figure 2b), followed by a 13% decline from 77.6 kg N ha^{-1} yr^{-1} in 2000 to 67.5 kg N ha^{-1} yr^{-1} in 2009 due to decreased fertilizer N application and agricultural biological N fixation from decreased crop cultivation area (∼44%). The contrasting trend between NANI and riverine TN export observed in the 2000s implies a lag effect in NANI export to rivers[17,31−33] and/or a contribution of another N source that is not considered in NANI (such as soil N release),[40−42] and/or an increased fractional export of NANI to the river due to changes of climate[24−27] and/or land-use.[7,9]

A cross-correlation analysis indicated that annual riverine TN flux was not only related to NANI during the current year, but also to NANI in the previous 6 years (Figure 3a), implying a 7-yr (current year plus previous six years) lag time of NANI to river N export, due to long transit times for N passing through the soil and vadose/groundwater zones to the river network.[15−19] The 7-yr time lag between NANI and riverine N export falls within the range estimated in previous studies of one year to several decades.[2,15,19,20] The magnitude of lag time is mainly dependent on hydrological and biogeochemical processes in the watershed.[17−20] Stable isotopic tracers (mainly ^{3}H) have shown that delivery times for surface runoff, soil water/shallow groundwater, and deep groundwater to river
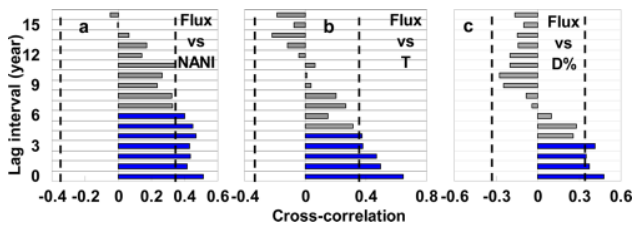
Figure 3. Cross-correlations between riverine TN flux and NANI (a), riverine TN flux and temperature (T) (b), and riverine TN flux and drained agricultural land percentage (D%) (c) in the Yongan River watershed over the 1980−2009 period. Dotted perpendicular lines denote the critical values for significant level ($p < 0.05$).

systems are on the order of days, years, and decades, respectively.[17,32] Incorporation of N into soil organic matter and subsequent release of this N for potential leaching to the hydrosphere is estimated to require one year to decades.[18−20] Although there are no artificial dams along the Yongan River, backwater pool and reservoirs within river systems are another cause for delaying N export by rivers. The 7-yr lag time for NANI delivery to the river determined from the cross-correlation analysis is believed to be an average of all these processes delaying N delivery from the watershed to the river outlet. Moreover, riverine TN flux was correlated with the previous 4 years of temperature and 3 years of drained agricultural area (Figure 3b and c), which are likely due to the time required for increasing temperature and the renovated drainage channel network (modernized in the early 2000s for this watershed) to affect soil organic N mineralization and N delivery to rivers.[7,16,19,20]

Due to the lag time, the 7-yr moving average NANI, 5-yr moving average temperature, and 4-yr moving average D% were shown to explain greater variability in annual riverine TN flux than the year-by-year series (Table 1). Analyses using other

Table 1. Results of Regression Analysis between Annual Riverine TN Flux (y) and Various Independent Variables (x) at Year-by-Year or Multiple Year Moving Average Scales in the Yongan River Watershed Over the 1980−2009 Period

independent variables	regression equations	R^2	n
NANI	$y = 4.541e^{0.0129x}$	0.27^a	30
7-yr moving averaged NANI	$y = 4.882e^{0.0116x}$	0.64^a	24
precipitation	$y = 1.745e^{0.0013x}$	0.50^a	30
the coefficient of variation for daily rainfall	$y = 8.1x - 2.03$	0.43^a	30
number of storm events	$y = 6.573e^{0.108x}$	0.42^a	30
discharge	$y = 4.899e^{0.01x}$	0.49^a	30
efficient drainage area percentage (D%)	$y = 30.1x + 4.0$	0.29^a	30
4-yr moving averaged D%	$y = 28.7x + 4.3$	0.52^a	27
developed land percentage	$y = 514.7x - 3.4$	0.40^a	30
temperature	$y = 0.0445e^{0.312x}$	0.42^a	30
5-yr moving average temperature	$y = 0.0437e^{0.314x}$	0.62^a	26

^{a}Significant $p < 0.01$.

multiple-year moving averages resulted in lower correlations (SI, Part VI, Table S8). These results suggest that the 7-yr average for NANI, 5-yr average temperature, and 4-yr average D% were best for developing a quantitative relationship between NANI and riverine TN flux, as well as for application in lumped watershed models such as export coefficient models, SPARROW, and PolFlow for this watershed. Such lag effects

for NANI on riverine TN export may partially explain the increasing riverine TN flux observed in the 2000s, despite a significant decline in NANI since 2000 (Figure 2a and b). Although no significant cross-correlations (thus no lag time) were found between riverine TN flux and precipitation, the coefficient of variation for daily rainfall, storm events, discharge, and developed land area percentage, the year-by-year correlations between each of these variables and TN flux were significantly higher than for NANI (Table 1), implying the importance of hydroclimate and land-use changes in further regulating residence time of N delivery from the landscape to river.[2,4,6,9]

Potential Effect of Soil N Release on Riverine TN Export. The 7-yr lag time for NANI export to the river (Figure 3a) and the contrasting trend between NANI and riverine TN export over the past 10 years (Figure 2) implies a potential contribution of another N source that is not directly considered in the NANI approach. Both soil organic matter (12.4% or 3.8 g kg^{-1} decrease) and total N (43.8% or 1.21 g kg^{-1} decrease) in the upper 20 cm layer of agricultural soils decreased significantly between 1984 and 2009 (Figure 4a). The decrease
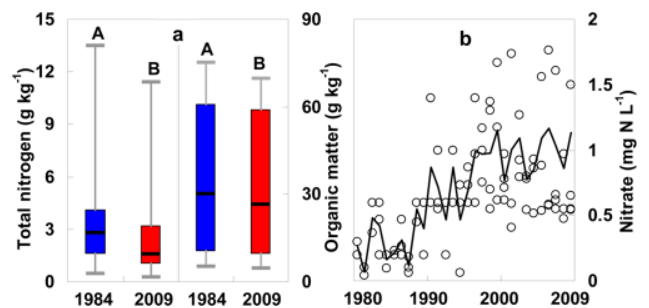

Figure 4. Soil total nitrogen ($n = 415$) and organic matter ($n = 305$) contents in the upper 20 cm of agricultural soils between years 1984 and 2009 (a) and river nitrate concentration ($n = 95$, black line denotes flow-adjusted concentration) during the low flow (baseflow) regime (70−100th interval) (b) in 1980−2009 in the Yongan River watershed. Capital letters above bars denote significant differences ($p < 0.01$).

in soil N content occurred in spite of these agricultural lands receiving large NANI (=fertilizer N input + atmospheric deposition + biological fixation−crop production): changed from 69.4 kg N ha^{-1} in 1984, to 183.4 kg N ha^{-1} 2000, and 134.1 kg N ha^{-1} in 2009, suggesting that N removal via crop production would be not the main cause for this decrease in soil N content. An estimated 270 kg N ha^{-1} during the study period was lost from the upper 20 cm layer of agricultural soils (SI, Part III) and made available for denitrification, leaching to deeper soils and groundwater, and river export. Soil N release was expected to be enhanced during the 1980−2009 period, especially for 2000−2009, considering the rapid increase in drained agricultural land area (∼50% increase) in the 2000s (SI, Part III, Figure S5) and the significant temperature increase (∼1.2 °C increase) since 1995 (SI, Part I, Figure S1). Similar effects of increasing drainage and temperature as well as continuous application of chemical N fertilizers (Figure 2b) on N export are well understood and would increase soil N release due to increased soil aeration and mineralization rate.[7,24−27] The resulting loss of soil organic matter further reduces the soil potential to immobilize available N, which in turn increases the

risk of N leaching to the vadose zone and groundwater as well as the river.[7,18,26]

Due to the unavailability of annual soil property data for various landscapes, we cannot determine soil N status dynamics over the study period (especially for the 2000s) and annual soil N release amount for the entire watershed. However, the significant decrease of agricultural soil N (Figure 4a) enhanced by warmer temperature and improved agricultural drainage implies that other watershed soils, especially woodland soils (located in high elevation areas and linked with agricultural lands, Figure 1) due to progressive N saturation from increasing atmospheric N deposition,[43] have the potential to release additional N. Accordingly, N storage in deeper soils and aquifer/groundwater would increase due to enhanced N leaching from the upper soil layer, decreasing soil organic matter, and increasing NANI over the past 30 years, resulting in an increase of N export via subsurface runoff and groundwater to rivers.[17,39,44,45] This statement is supported by the 2.7-fold increase of annual average flow-adjusted nitrate concentration from 1980 to 2009 with a 23% increase from 2000 to 2009 (nitrate represented 54% of measured TN in 1980−2009 on average, SI, Part II) during the low flow regime (baseflow) when the river water is mainly supplied by groundwater inputs (Figure 4b). This considerable increase in baseflow nitrate concentrations further supports the role of groundwater in contributing to the observed lag effect of NANI on river export (Figure 3a). In addition to river export and storage in deeper soils and groundwater, soil released N can be removed by enhanced denitrification due to increasing temperature.[13] Therefore, soil N release that was enhanced by human disturbance and climate warming is another potential source of riverine TN and should be considered in watershed N budgets.

Regression Models for Riverine TN Export. The analyses reported above suggest that long-term NANI and riverine TN export dynamics are regulated by the lag effect, soil organic N release, and hydroclimate. Due to the unavailability of annual soil data for various landscapes (thus we cannot directly address the dynamic relationship between soil N release mass and riverine TN flux), a combination of annual average temperature and drained agricultural land area percentage (D%) was adopted to represent the contribution of soil N release due to their influence on enhancing soil mineralization and N leaching.[7,24−27] Considering the lag effect, we utilized the 7-yr moving average of NANI ($NANI_{0-6}$, kg N ha^{-1} yr^{-1}), 5-yr moving average of temperature (T_{0-4}, °C), and 4-yr moving average of D% ($D\%_{0-3}$) to develop the empirical model for riverine TN flux. As this study (Table 1) and previous studies have shown,[2,6,8] the relationship between riverine N export (L, kg N ha^{-1} yr^{-1}) and NANI is best described using an exponential function in the form:

$$L = \alpha Q^{\beta_1} \exp(\beta_2 NANI_{0-6} + \beta_3 T_{0-4}D\%_{0-3}) \quad (1)$$

where Q is annual average discharge (m^3 s^{-1}), and α, β_1, β_2, and β_3 are fitting parameters. Regression analysis (SPSS version 16.0, SPSS Inc., 2002) was applied to calibrate these four parameters (SI, Part VI, Table S9) after a logarithmic transformation of eq 1, resulting in the following model:

$$L = 0.081Q^{0.89}\exp(8.7 \times 10^{-3}NANI_{0-6} + 0.147T_{0-4}D\%_{0-3}) \quad (2)$$

Equation 2 accounted for 96% of the variation in annual TN fluxes over the 1980−2009 period (Figure 5a). All calibrated
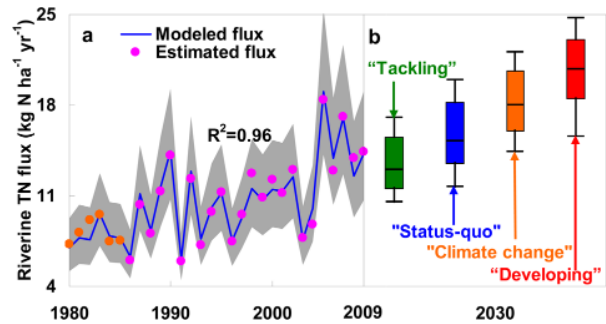
Figure 5. LOADEST estimated riverine TN flux versus modeled values from eq 2 in 1980−2009 (a) and predicted TN fluxes for 2030 under four scenarios (b) in the Yongan River watershed. The orange circles for fluxes in 1980−1984 were predicted using average NANI, drained agricultural area percentage, and temperature during the present year and previous 1−5 years. Shadow area denotes 95% confidence interval of modeled flux. Box plot denotes 97.5%, 75%, 50%, 25%, and 2.5% confidence of predicted flux.

parameter values were highly statistically significant ($p < 0.001$, SI, Part VI, Table S10). Average errors for TN flux prediction accuracy were <5%, and the interquartile range of each year was relatively symmetrical, typically ranging from −25% to +25%, although an over prediction was noted for 2006 and under predictions were noted for 1998 and 2000 (Figure 5a). This model agreement is comparable or superior to similar models developed for other watersheds[2,4,6,8] and lumped watershed models for N smiulations[12−15] ($R^2 = 0.67−0.95$). Considering the complexities of N delivery across watershed landscapes, the modeled results are very reasonable and can successfully predict riverine N export. As expected, the performance of the multiple-year moving average model was better than the year-by-year model ($R^2 = 0.96$ vs 0.84 and relative error = ± 5% vs ±10%) (SI, Part VI, Table S9). When we replaced the $T_{0-4}D\%_{0-3}$ term in eq 1 with various combinations of variables listed in Table 1, the performance of the resulting models was inferior (SI, Part VI, Table S9). These results further indicated the importance of the lag effect and soil N release on riverine TN export.

Riverine N Source Apportionment. Based on eq 2, we were able to estimate the riverine TN flux derived from natural background sources (L_N, kg N ha^{-1} yr^{-1}), soil N pool (L_S, kg N ha^{-1} yr^{-1}), and NANI (L_{NANI}, kg N ha^{-1} yr^{-1}) as follows:

$$L_N = 0.081Q^{0.89} \quad (3)$$

$$L_S = 0.081Q^{0.89}[\exp(0.147T_{0-4}D\%_{0-3}) - 1] \quad (4)$$

$$L_{NANI} = 0.081Q^{0.89}[\exp(8.7 \times 10^{-3}NANI_{0-6} + 0.147T_{0-4}D\%_{0-3}) - \exp(0.147T_{0-4}D\%_{0-3})] \quad (5)$$

For the Yongan River watershed, estimated riverine TN flux derived from natural background sources was 77.6 kg N ha^{-1} or 2.6 kg N ha^{-1} yr^{-1} and contributed to 24% of the observed cumulative TN export in 1980−2009. This estimate falls within the range observed in other watersheds, that is, 1.07−2.78 kg N ha^{-1} yr^{-1}, but is larger than the median value for those watersheds evaluated.[3,4,6] It is plausible that the higher runoff in this watershed (mean = 923; range = 499−1582 mm yr^{-1}) than the other watersheds (<800 mm yr^{-1}) results in higher background N export since it was a function of discharge in

the this watershed ($R^2 = 0.34$, $p < 0.01$), as well as others.[6] The soil N pool was estimated to represent 108.4 kg N ha^{-1} or 3.6 kg N ha^{-1} yr^{-1} and contributed 35% of the observed cumulative TN export, which is supported by the observed net N release from the upper 20 cm layer of agricultural soils and rapid increase of nitrate concentration during the baseflow period between 1980 and 2009 (Figure 4). In addition to the lag effect, this contribution from the soil N pool partially explains the increasing riverine TN export observed following the decline of NANI since 2000 (Figure 2).

Total NANI accounted for 129 kg N ha^{-1} or ~41% of the observed cumulative riverine TN flux. This flux represented ~8% (range = 5−12%) of NANI during the study period, which is comparable with previous estimates of 5−40%,[4,9,10,46] but is lower than the median value (~20%) for those watersheds evaluated. This may be due to the lack of consideration for soil N release in previous studies and high N retention or assimilation capacity resulting from the high percentage of forest (~67%) in this watershed. Estimated fraction (F) of the 7-yr average NANI exported by the river showed a 58% increase from 1980 to 2009 ($F = 0.0011x + 0.0536$, $R^2 = 0.27$, $p < 0.01$, x is year number), which partially explains the contrasting trend observed between NANI and riverine TN flux in the 2000s (Figure 2). Increasing export fraction is likely due to increasing temperature, the coefficient of variation for daily rainfall (CVR), and storm events (SE), as well as increases in drained agricultural area percentage (D%) and developed land area percentage (C%) over the past 30 years (SI, Part I, Figure S1). Increasing CVR, SE, C%, D%, and discharge or precipitation is expected to increase the fractional export of NANI (Table 2) via decreasing water residence time

Table 2. Results of Regression Analysis between Fractional Export of 7-yr Average NANI by River (y) and Various Independent Variables (x) at Year-by-Year or Multiple Year Average Scales in the Yongan River Watershed over the 1980-2009 Period[a]

independent variables	regression equations	R^2	n
precipitation	$y = 0.0125e^{0.0012x}$	0.58[b]	30
discharge	$y = 0.0324e^{0.0104x}$	0.53[b]	30
CVR	$y = 0.0328e^{0.481x}$	0.36[b]	30
number of storm events	$y = 0.0464e^{0.0989x}$	0.44[b]	30
4-yr averaged D%	$y = 0.0395e^{2.633x}$	0.25[b]	27
developed land percentage	$y = 2.8x - 0.004$	0.32[b]	30
5-yr average temperature	$y = 0.02x - 0.28$	0.28[b]	26

[a]CVR denotes the coefficient of variation for daily rainfall; D% denotes drained agricultural land percentage. [b]Significant $p < 0.01$.

in the landscape that enhances N flushing, increases the runoff-to-infiltration ratio, and decreases in-stream N loss efficiency.[4,6,45] Increasing temperature enhanced the mineralization of residual NANI accumulated in soil organic matter,[25,26] resulting in increased N leaching to groundwater and the river. These results imply that hydoclimate change can enhance riverine TN export through increasing fractional export of NANI.

The estimated N imbalance between accumulated NANI (1837 kg N ha^{-1}) and modeled riverine TN export derived from NANI (129 kg N ha^{-1}) over the study period represents 92% of the NANI and may result from leaching to deeper soils and aquifers, denitrification, wood product export, and forest biomass storage.[40,41] Leaching to groundwater can represent

about 2−6% of annually applied fertilizer N according to field studies conducted in surrounding regions,[37,47] which is supported by the rapid increase of baseflow nitrate concentrations over the past 30 years (Figure 4). If 12−23% of NANI was removed by wood products and stored in forest ecosystems as estimated for American watersheds[40] (this is coincident with a 60% increase in forest foliar N content observed in eastern China from 1980 to 2009),[43] denitrification would by difference account for a maximum of 63−78% of NANI. This denitrification percentage is comparable with the sum of agricultural land denitrification (i.e., 36.4−48.2% for total N applied to agricultural lands)[37,38,46] and in-stream denitrification (i.e., 10−35% of total N input to rivers) determined using modeling approaches[5,47] in surrounding regions. Denitrification would be expected to increase during the study period due to an increase in temperature, a 76% increase in atmospheric NO$_y$ (sum of NO, NO$_2$, HNO$_3$, and NO$_3^-$) deposition over the past 30 years (Figure 2b), and increasing nitrate concentrations as a substrate for denitrification (Figure 4b). While N removal via transboundary water withdrawal does not occur in this watershed, it could be another potential sink for NANI in other watersheds.

Forecasting Future Riverine N Exports. Using eq 2, riverine N exports in response to changes in expected NANI levels, climate, and development of artificially drained agricultural lands were predicted for the 2010−2030 period using four possible future scenarios (SI, Part VII; Figure 5b). The "status-quo" scenario projects a 5.1% increase in NANI to the Yongan River watershed coupled with a 1.1 °C increase in temperature between 2009 and 2030 and predicted a 6% increase of riverine TN export in 2030. Under the "tackling" scenario NANI in 2030 would be 15.2% less than 2009, which predicted a 13% decrease of riverine N export in 2030 with no changes in climate and drained agricultural land area. Under the "developing" scenario NANI would increase 23.2% between 2009 and 2030, resulting in a 45% increase of riverine TN export enhanced by a 4% increase in discharge, 1.1 °C increase in temperature, and 23.2% increase in drained agricultural land area relative to 2009. Under the "climate change" scenario, although NANI and drained agricultural land area in 2030 remained the same as 2009, riverine TN flux would increase 25% due to a 4% increase in discharge and 1.1 °C increase in temperature, consistent with predictions for the Susquehanna River basin (U.S.) where a 2% increase in discharge resulted in a 17% increase in riverine N flux by 2030 with no change in N inputs.[13] This response is mainly due to greater fractional delivery of NANI and soil N release as water discharge and temperature increase (Table 2).

Although these predictions are subject to several uncertainties associated with changes in future N inputs, climate, and soil organic N pools, these predicted results roughly represent the upper and lower bounds for future riverine N fluxes in response to anthropogenic activities and climate change, providing a baseline for adopting relevant N management strategies. In terms of effective N source management, reducing riverine TN flux should primarily focus on decreasing atmospheric N deposition and fertilizer N application based on the sensitivity analysis for eq 2 (SI, Part VI, Figure S10). Due to the lag effect, it is expected that reductions in NANI would take at least 7 years to be fully observed in riverine TN export. The lag effect and the contribution of the soil N pool observed in this study suggest that water N pollution control measures and evaluations should consider the time delay resulting from

historical N inputs, which is the likely cause of increasing riverine N exports in many areas where significant declines in NANI have been achieved.[15,17,31−33] Given the stronger dependence on discharge (SI, Part VI, Figure S10 and Table 1) than on NANI, a more immediate response for riverine TN export reduction may result from N delivery interception strategies (e.g., wetlands, riparian buffers)[47] rather than N source input reduction. Considering the potential impact of global climate change on enhancing river N export, the influence of climate change should be considered as a part of management efforts to control N pollution.

Implications for Watershed N Modeling and Management. This study demonstrates the importance of the N-leaching lag effect, soil N release, and climate change in regulating watershed NANI and riverine N export dynamics. Cross-correlation analysis provides a simple and efficient method for determining the appropriate length of the multiyear record that should be used to estimate average N inputs or other influencing factors in developing the relationship between NANI and riverine N export as well as applying lumped watershed models. Soil N release can be enhanced by warmer temperature and improved agricultural drainage systems and is a considerable source of riverine TN flux that should be considered in watershed N budget analysis. Climate change enhances the riverine TN export through increasing fractional export of NANI. The lag effect, soil N release, and climate change are expected to cause increasing riverine N exports even after a significant decline in NANI has been achieved. Legacy N associated with the lag effect and soil N release and the impact of climate change must be rigorously considered in developing and evaluating management measures to control aquatic N pollution.

■ ASSOCIATED CONTENT

ⓢ Supporting Information
Part I: Detailed description of the Yongan River watershed. Part II: Riverine TN flux estimate. Part III: Soil characteristics and management. Part IV: NANI calculation. Part V: Cross-correlation analysis. Part VI: Regression and sensitivity analyses for annual riverine TN export. Part VII: Scenarios for forecasting future riverine TN flux. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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■ ABBREVIATIONS

NANI net anthropogenic nitrogen input
TN   total nitrogen
D%   drained agricultural land percentage
C%   developed land percentage
CVR   coefficient of variation for daily rainfall
SE   storm events

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