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Modeling forest/agricultural and residential nitrogen budgets and riverine export dynamics in catchments with contrasting anthropogenic impacts in eastern China between 1980–2010

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ABSTRACT

This study quantified the long-term response of riverine total nitrogen (TN) export to changes in net anthropogenic nitrogen inputs to forest/agricultural ($NANI_{FA}$) and residential ($NANI_R$) systems across three catchments affected by low (LD), medium (MD), and high (HD) human impacts in eastern China. Annual $NANI_{FA}$ increased by 63–87% in 1980–1999, followed by 0% (LD), −23% (MD) and −40% (HD) changes of $NANI_{FA}$ in 2000–2010, resulting in a net increase of 56–78% in $NANI_{FA}$ in 1980–2010. Annual $NANI_R$ increased by 101–152% in the three catchments in 1980–2010. Land-use showed a 58–65% increase in developed land area (D%) and a 96–108% increase in agricultural lands with improved drainage systems (AD%) over the study period. In response to changes in $NANI_{FA}$, $NANI_R$ and land-use, riverine TN flux continuously increased 3.0- to 6.1-fold in the three catchments over the past 31 years. For each catchment, an empirical model incorporating annual $NANI_{FA}$, $NANI_R$, water discharge, D%, and AD% was developed ($R^2 = 0.93 - 0.97$) for predicting and quantifying sources of annual riverine TN fluxes. The model estimated that $NANI_{FA}$, $NANI_R$ and other N sources (e.g., natural background, legacy, and industrial N sources) contributed 27–90%, 0–45%, and 10–28% of riverine TN fluxes, respectively. Model results were consistent with spatio-temporal changes of riverine chloride, ammonium, nitrate, dissolve oxygen and pH, as well as changes in available N levels in agricultural soils. In terms of N source management, reduction of $NANI_{FA}$ in catchment LD and $NANI_R$ in catchment HD would have the greatest impact on reducing riverine TN fluxes. Furthermore, changes in land use and climate as well as legacy N should be considered in developing N pollution control strategies.

1. Introduction

Human activities associated with food and energy production have greatly elevated nitrogen (N) bioavailability to an extent that exceeds the assimilative capacity in many terrestrial ecosystems, often leading to large increases in N fluxes to waters (Kopáček et al., 2013; Wang et al., 2014). Enrichment of N leads to eutrophication of surface waters causing degradation of aquatic ecosystems, such as toxic algal blooms, low dissolved oxygen, depletion of fish populations, and loss of aquatic biodiversity (Kettering et al., 2012; Vogt et al., 2015; Hofmeier et al., 2015). To effectively guide watershed management to control N pollution, it is essential to quantify the response of riverine N export to changes in sources and levels of anthropogenic N inputs (Hayakawa et al., 2009; Chen et al., 2014a).

Nitrogen budgets are useful for evaluating impacts of human activities on the N cycle by relating anthropogenic N inputs to outputs (Hayakawa et al., 2009; Kettering et al., 2012; Wang et al., 2014). Net anthropogenic nitrogen input (NANI) is a budgeting approach that sums annual N contributions from atmospheric deposition, fertilizer application, agricultural fixation, seed input, and net import/export in feed and food (Hong et al., 2013; Han et al., 2014). The NANI approach has been applied to many watersheds across Asia (Hayakawa et al., 2009; Han et al., 2014; Chen et al., 2014a; Huang et al., 2014; Gao et al., 2014, 2015; Swaney et al., 2015), America (McIsaac et al., 2001; Boyer et al., 2002; Han et al., 2009; Hong et al., 2013), and Europe (Billen et al., 2009; Kopáček et al., 2013). It is a simple yet powerful approach to evaluate net N inputs

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from anthropogenic sources to terrestrial ecosystems, as well as an effective tool to explain among-watershed or among-year variations in riverine N exports. However, the relationship between NANI and riverine N export is additionally influenced by variations in hydroclimate and land management activities, as well as progressive N saturation of terrestrial ecosystems (McIsaac et al., 2001; Han et al., 2009; Howarth et al., 2012; Swaney et al., 2012; Kopáček et al., 2013; Chen et al., 2014b; Huang et al., 2014). It is commonly observed that years with higher precipitation or river discharge export a higher fraction of NANI via rivers than drier years (Han et al., 2009; Howarth et al., 2012). Furthermore, the export fraction of NANI via rivers can be enhanced by improved agricultural drainage systems (e.g., tile drainage, McIsaac and Hu, 2004; Kopáček et al., 2013). Previous studies also demonstrate a larger fractional export of NANI by rivers when NANI exceeds some threshold value (e.g., 10.7 kg N ha^{-1} yr^{-1}, Howarth et al., 2012), which corresponds to NANI exceeding the N assimilative capacity of terrestrial and aquatic ecosystems (McIsaac et al., 2001; Han et al., 2009; Chen et al., 2014b; Gao et al., 2014). As a result, changes of climate, land management, and the degree of N saturation have a strong potential to enhance riverine N export (McIsaac et al., 2001; Huang et al., 2014; Øygarden et al., 2014). Importantly, the influence of climate change, land-use change and progressive N saturation is difficult to detect from short-term (several years) records, instead requiring a long-term (several decades) record of NANI and riverine N export dynamics.

For a watershed, the NANI components of chemical fertilizer, atmospheric deposition, biological fixation and seed input are the primary N inputs to forest and agricultural systems, while residential systems mainly receive N from human and animal wastes. In terms of N delivery pathways, N exports from forest and agricultural landscapes to the river network are mainly via diffuse runoff and leaching (non-point sources) (Chen et al., 2009), while a portion of N from residential systems enters the river network via direct sewage discharge (point sources) (Gao et al., 2014; Huang et al., 2014). In addition, the greater impervious surface area in residential systems further enhances N delivery efficiency (Groffman et al., 2004; Kaushal et al., 2008). As a result, residential systems have a higher potential to export NANI than forest/agricultural systems. This is especially true in developing countries where agricultural subsurface drainage and efficient treatment of residential wastewater are both often lacking (Yan et al., 2011; Chen et al., 2013). Therefore, it is valuable to separate watershed forest/agricultural and residential N budgets to effectively identify their contrasting export fractions and relative contributions to riverine N fluxes.

Based on extensive data collection for three adjacent catchments subjected to low, medium and high levels of anthropogenic impacts in eastern China, this study provides a long-term (1980–2010) analysis of the response of riverine TN export to changes in forest/agricultural and residential N budgets, land use and climate. Specifically, this study (i) examines temporal and spatial variations of NANI to forest/agricultural ($NANI_{FA}$) and residential ($NANI_R$) systems, (ii) addresses temporal and spatial variations of riverine N fluxes; (iii) develops empirical models for linking $NANI_{FA}$ and $NANI_R$ to riverine TN fluxes, and (iv) identifies individual contributions from $NANI_{FA}$, $NANI_R$ and other sources (e.g., natural background, legacy and industrial N sources) to the riverine TN flux. This study improves the NANI budgeting methodology to separately estimate watershed $NANI_{FA}$ and $NANI_R$ budgets and identifies of their contributions to annual riverine TN flux. Such quantitative knowledge is essential for managers to determine which systems and sources should be targeted for N reduction.

2. Materials and methods

2.1. Study catchments

The three catchments in this study are located in the rapidly developing Taizhou region of Zhejiang Province, China (Fig. 1). The three rivers are tributaries of the Jiaojiang River, which is the third largest river of Zhejiang Province and flows into Taizhou Estuary and the East China Sea, a coastal area that commonly experiences hypoxia (Gao and Zhang, 2010). The climate is subtropical monsoon having an average annual temperature of 17.2 °C and

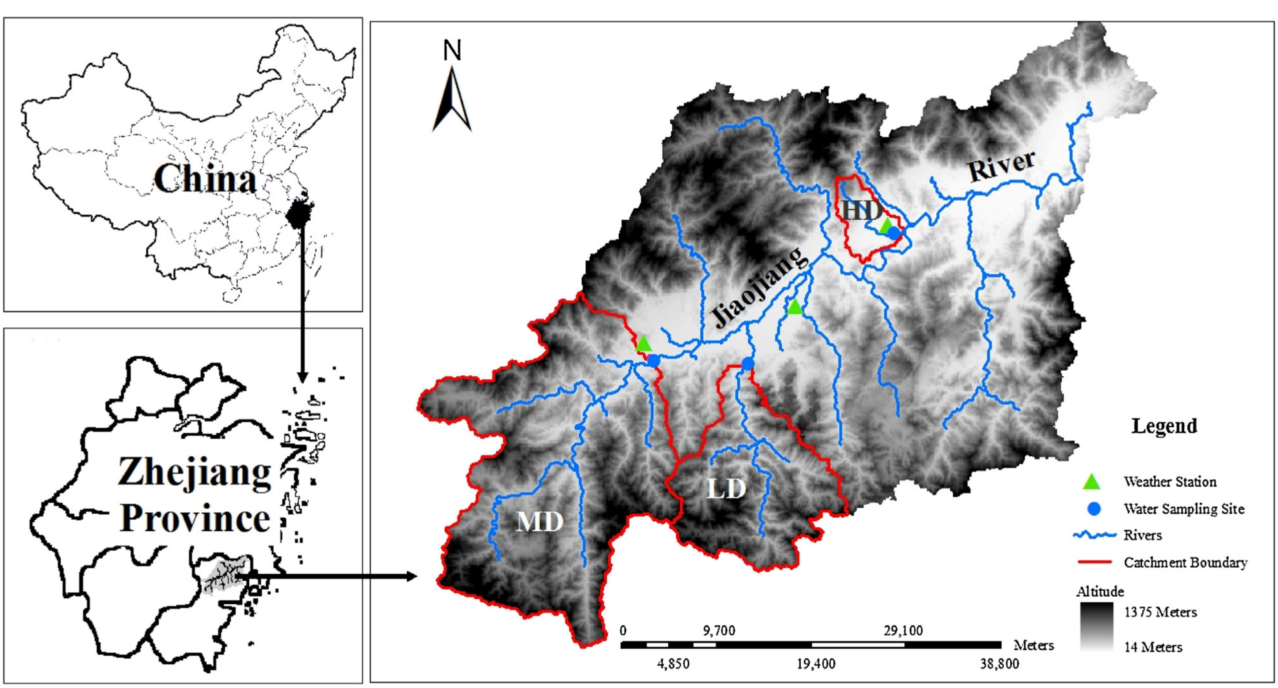

Fig. 1. The location of the three catchments affected by low (LD), medium (MD), and high (HD) levels of anthropogenic disturbance in Jiaojiang watershed in Zhejiang Province in eastern China.

average annual precipitation of 1395 mm. Due to the dominant volcanic, malmstone and mudstone bedrock lithologies, groundwater or base flow contributes ~45% of annual river water discharge in the upper Jiaojiang River watershed the investigation made by local Hydrology Bureau. Rainfall mainly occurs in May–September (~62%) with a typhoon season in July–September, while winter (December–February) is a major dry season (~12%). From 1980 to 2010, there were no significant trends ($p > 0.05$) in annual precipitation or river discharge in the three catchments (Appendix A, Fig. A1).

Considering the availability of relevant long-term data, this study selected three catchments within the Jiaojiang watershed to provide a range of anthropogenic impacts from agricultural activity and urbanization (Table 1). In terms of managed land area percentage (agricultural and developed lands), as well as agricultural drainage, human population and domestic animal density, the three catchments were classified into low (LD), medium (MD) and high (HD) levels of anthropogenic impacts. Except for catchment HD, catchments LD and MD have comparable slopes and altitudes due to their locations within the watershed (i.e., LD and MD are upstream watersheds and HD a mid-elevation watershed). The three catchments have similar precipitation and soil characteristics (Appendix B, Table B1). Between 1980 and 2010, average managed land area percentage was 4%, 9% and 26% for catchments LD, MD and HD, respectively. Correspondingly, natural forest (~90% coniferous and ~10% deciduous) and barren lands accounted for 96%, 91% and 74% of the entire catchment area for LD, MD and HD, respectively. Thus, LD may be considered as a reference catchment for examining progressive nitrogen saturation in a dominantly natural ecosystem over the study period. The average percentage of agricultural lands with efficient drainage systems was 12%, 14% and 35% for LD, MD, and HD, respectively (Table 1). Average population density was 74, 134 and 761 capita km^{-2}, while domestic animal density (normalized to an equivalent number of pigs according to N excretion rates; Table D.2) was 36, 65, and 153 capita km^{-2} for LD, MD, and HD, respectively.

Over the 31-year study period, human population within LD, MD, and HD increased by 25%, 32%, and 30%, while managed land area increased by 39%, 43%, and 24%, respectively. The economic role of agriculture has been increasingly replaced by industry since the 1990s, resulting in a remarkable reduction in cropland cultivation (13–46%) as well as N fertilizer use (42–44%) since 2000 (Table 1). Due to reduction in cropland and increasing availability of chemical fertilizer, recycled animal and human excreta for fertilizing croplands also decreased from ~93% in 1980 to ~21% in 2010 (Appendix D, Table D.2). The remaining animal wastes were removed via artificial treatments (e.g., landfills, incinerators, biogas digesters, septic-tanks or wastewater treatment plants) and direct discharge to the environment (e.g., residential soils and streams). Agricultural land area irrigated and drained with improved cement channels and pipes increased by 96–108% since 1980 (Appendix B, Fig. B.1).

2.2. Data sources and analysis

Historical water quality records ($n = 170 - 231$; TN, ammonium, nitrate, dissolved oxygen, chloride, and pH) and daily river discharge at the three sampling sites (Fig. 1) between 1980 and 2010 were obtained from the local Environmental Protection Bureau and Hydrology Bureau, respectively (see Appendix C for field and laboratory protocols). Available N contents (extractable $NH_4^+ + NO_3^-$), pH, and bulk densities in the upper 20-cm layer of agricultural lands measured at the same location following crop harvest in 1984 and 2009 were provided by the local Agriculture Bureau (Appendix B). Data for N sources and sinks used to estimate N budgets and land use from 1980 to 2010 were derived from local statistics yearbooks (Appendix D). All statistical analyses were performed using SPSS statistical software (version 16.0, SPSS Inc., Chicago, IL, USA).

2.3. Nitrogen budget calculations and uncertainty analysis

This study made two modifications to the standard NANI budgeting approach (Hong et al., 2013; Han et al., 2014) by (i) considering the influence of increased soil available N on the protein content (i.e., N content) of crops for estimating N removal via harvest (Kopáček et al., 2013), and (ii) adjusting atmospheric NO_x deposition with NO_x emission from local crop residue burning (Yan et al., 2006; Yan et al., 2011). NANI (kg N ha^{-1} yr^{-1}) was

Table 1
Characteristics of natural conditions and human activities for the three catchments affected by low (LD), medium (MD), and high (HD) levels of anthropogenic disturbance in 1980 – 2010.

Catchment		LD (218 km^2)			MD (547 km^2)			HD (35 km^2)		
		1980s	1990s	2000s	1980s	1990s	2000s	1980s	1990s	2000s
Agricultural land (%)		2.9	2.9	3.4	6.8	6.5	8.7	17.5	17.4	20.7
Developed land (%)		0.7	0.7	0.9	1.3	1.3	1.7	6.9	6.8	9.1
Nature forest (%)		75.0	75.0	73.1	71.2	71.2	69.3	44.3	52.8	59.6
Barren lands (%)		21.4	21.4	22.6	20.7	21.0	20.3	31.3	23.0	10.6
Soil groups	Red soil	71%			63%			68%		
	Yellow soil	17%			15%			19%		
	Others	12%			22%			13%		
Slope		24.6°			20.5°			7.5°		
Altitude (m)		546.2			537.7			138.7		
Cultivated crop land (km^2)		19.5	17.5	15.8	97.6	92.0	76.2	13.9	13.3	8.6
Chemical fertilizer (ton N yr^{-1})		128	195	162	785	1158	1021	125	193	158
Precipitation (mm yr^{-1})		1388	1438	1483	1278	1331	1313	1420	1488	1480
River discharge (m^3 s^{-1})		6.4	6.8	6.2	16.0	17.1	15.6	1.0	1.1	1.0
Population (capita km^{-2})		68	74	79	122	130	148	704	744	828
Domestic animal (capita km^{-2})		42	31	35	74	70	53	166	159	136
Runoff coefficient		0.66	0.68	0.60	0.65	0.65	0.60	0.72	0.73	0.67
Percentage of agricultural lands with improved drainage		10%	9%	16%	12%	10%	20%	30%	27%	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; other soil types include purple soil, lithological soil, skeleton soil and fluvo-aquic soil; cultivated crop land denotes annual area planted to crops; runoff coefficient denotes the ratio between annual total runoff depth and precipitation.

calculated as the sum of five major components: net atmospheric NO_x deposition (NAD), chemical fertilizer N application (CF), agricultural N fixation (ABF), seed N input (SI), and net N in food/feed import/export (NFFI):

$$NANI = CF + NAD + SI + ABF + NFFI \quad (1)$$

The NFFI ($kg\,N\,ha^{-1}\,yr^{-1}$) was composed of crop and livestock production and N consumption by livestock and humans (Hong et al., 2013; Han et al., 2014):

$$NFFI = HC + AC - (G - GL) - (AP - APL) \quad (2)$$

where HC is human consumption, AC is animal consumption, G is harvested grain, GL is grain loss due to pests, spoilage and processing, AP is animal products, and APL is spoilage and inedible components of animal products.

To examine differences in N delivery efficiencies, NANI ($kg\,N\,ha^{-1}\,yr^{-1}$) was divided into separate budgets for forest/agricultural ($NANI_{FA}$) and residential ($NANI_R$) systems:

$$NANI = NANI_{FA} + NANI_R \quad (3)$$

Forest/agricultural land use dominated (>65% of total catchment area) for all three catchments (Table 1); thus NAD was fully considered as a new input for the forest/agricultural system:

$$NANI_{FA} = CF + NAD + SI + ABF + RAW + RDW - G - RF - NB \quad (4)$$

where RAW is recycled animal wastes for fertilizing agricultural lands, RDW is recycled domestic waste for fertilizing agricultural lands, and RF is crop residual used as fodder. $NANI_R$ was then estimated as follows:

$$NANI_R = HC + AC + GL + APL - RAW - RDW - AP \quad (5)$$

Detailed descriptions of individual N sources and sinks as well as the parameters used in estimating $NANI_{FA}$ and $NANI_R$ are available in Appendix D. To gain insight into the uncertainty of $NANI_{FA}$ and $NANI_R$ estimates, an uncertainty analysis was performed using Monte Carlo simulation (Appendix D). In accordance with previous studies (Yan et al., 2011; Ti et al., 2012; Huang et al., 2014), we assumed that all parameters used in estimating $NANI_{FA}$ and $NANI_R$ followed a normal distribution with a coefficient of variation of 30% in performing the Monte Carlo simulation. A total of 10,000 Monte Carlo simulations were performed to obtain the mean and 95% confidence interval for annual $NANI_{FA}$ and $NANI_R$.

2.4. Riverine N flux estimate

To estimate annual riverine TN, ammonium, and nitrate fluxes based on the discrete concentration records for each sampling site, the LOADEST model was applied for predicting daily fluxes (Appendix C). The calibrated LOADEST model resulted in high R^2 values ($R^2 = 0.78 - 0.96$, $p < 0.001$) and low average relative errors (±4–±15%) between measured and modeled values. As a conservative indicator for sewage (Jarvie et al., 2012), riverine chloride concentrations in the low flow regime (the lowest 30% of flow records, Chen et al., 2013) when there is no runoff input and limited dilution effect were extracted to indirectly address changes in sewage discharge in 1980–2010. Nitrogen loss via surface runoff is limited and NH_4-N (NH_4^+ or particle N has limited mobility through soil profiles) is commonly sourced to sewage discharge during the low flow regime (Swaney et al., 2012; Huang et al., 2014). Thus, riverine NO_3-N concentrations in the low flow regime (water mainly supplied by groundwater as base flow) were extracted to indirectly address changes in the nitrogen concentration of groundwater in 1980–2010 (Chen et al., 2014a,b).

3. Results

3.1. Long-term changes in nitrogen budgets

Over the 1980–2010 period, average annual net anthropogenic N inputs (NANI) to catchments affected by low (LD), medium (MD) and high (HD) levels of human disturbance were 19.8 ± 3.5, 34.4 ± 6.1, and 93.4 ± 15.9 $kg\,N\,ha^{-1}\,yr^{-1}$, respectively (Fig. 2). NANI to catchments LD, MD, and HD rapidly increased by 76%, 91% and 87% from 1980 to 1999, respectively. From 2000 to 2010, NANI in LD was relatively steady, while NANI in MD and HD decreased by 8% and 19%, respectively, resulting in a net increase of 51–78% for the three catchments over the 31-year study period.

In terms of individual sources, although chemical fertilizer input was a major source for each catchment, it decreased by 42–57% since 2000 due to a decrease (38–50%) in cropland area (Table 1). Net atmospheric NO_x deposition increased 2.8 ~ 9.8-fold between 1980 and 2010. Although net food/feed input was relatively steady in LD, it increased by 74% and 118% in MD and HD, respectively. Total input via agricultural biological N fixation and seed input was relative steady for LD and MD, but decreased in HD over the past 31 years.

Of cumulative NANI to LD, MD, and HD between 1980 and 2010, 67%, 66% and 53% were added to forest/agricultural systems ($NANI_{FA}$), while the remaining 33%, 34%, and 47% of N inputs originated from residential systems ($NANI_R$), respectively (Fig. 2). $NANI_{FA}$ increased 87%, 72%, and 63% in 1980–1999 for LD, MD, and HD, respectively, while remaining steady in LD and decreasing 23% and 40% in MD and HD in the 2000–2010 period, resulting in a net increase of 56–78% in $NANI_{FA}$. $NANI_R$ increased 101–152% over the

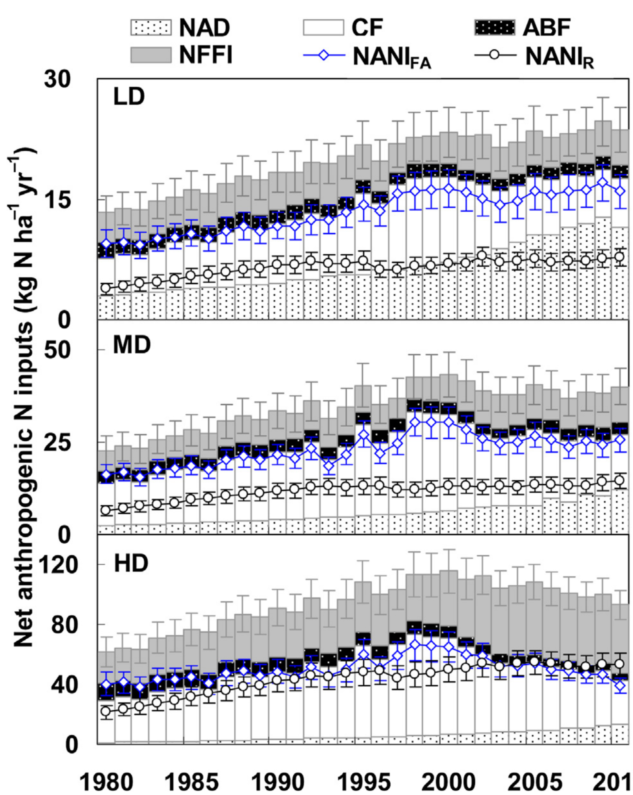

Fig. 2. Historical trends of NANI from net atmospheric deposition (NAD), chemical fertilizer (CF), agricultural biological fixation (ABF), net food and feed import (NFFI); seed input (SI) was <1% of input and is not shown; and NANI to forest/agricultural ($NANI_{FA}$) and residential ($NANI_R$) lands in the three catchments affected by low (LD), medium (MD), and high (HD) levels of anthropogenic disturbance over the 1980–2010 period. Error bars denote the 95% confidence intervals for NANI, $NANI_{FA}$, and $NANI_R$.

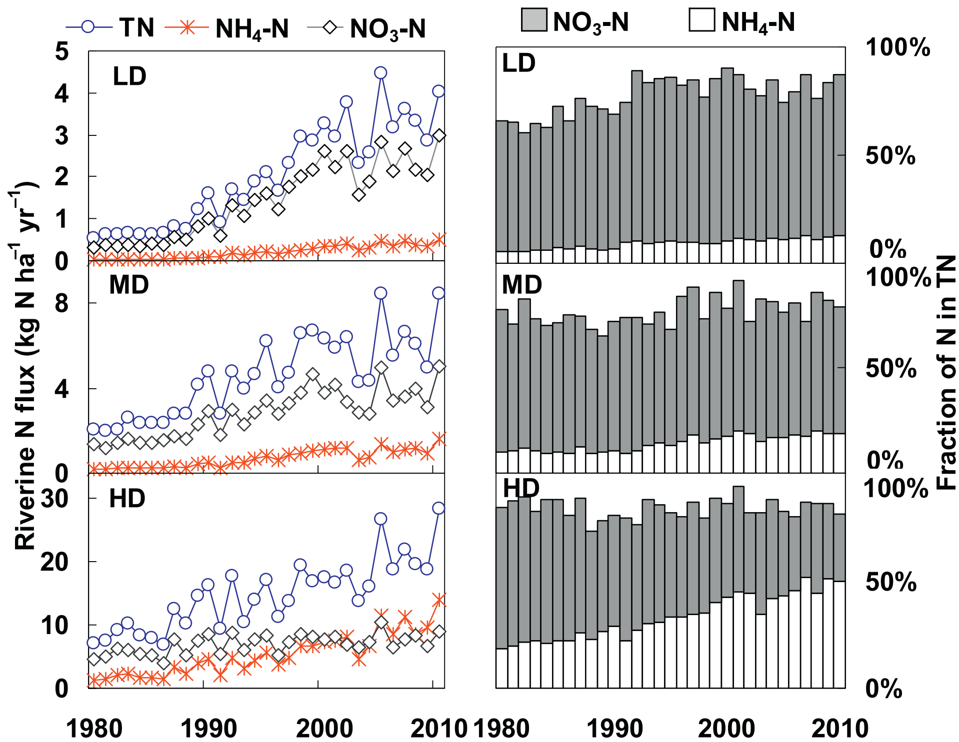

Fig. 3. Historical trends in riverine TN, NH_4-N, and NO_3-N fluxes (left) and contributions of NH_4^+ and NO_3^- forms to TN (right) in the three catchments affected by low (LD), medium (MD), and high (HD) levels of anthropogenic disturbance over the 1980–2010 period.

31-year study period due to a 48–58% increase in N consumption by humans and a ~75% decrease in recycled animal and human excreta for fertilizing croplands (Appendix D, Table D.2). Spatially, LD and HD had the lowest and highest $NANI_{FA}$ as well as $NANI_R$, respectively.

3.2. Long-term changes in riverine N export, water quality and soil available N level

Over the 1980–2010 period, average annual riverine TN fluxes at the LD, MD, and HD catchment outlets were 2.0 ± 1.2, 4.6 ± 1.9, and 14.6 ± 5.5 kg N ha^{-1} yr^{-1}, respectively (Fig. 3). For all three catchments, annual riverine TN, NO_3-N, and NH_4-N fluxes increased by 2.1 ~ 7.6-fold, 0.6 ~ 9.6-fold, and 6.7 ~ 19.2-fold over the 31-year study period, respectively. Corresponding to the spatial distribution of NANI/$NANI_{FA}$/$NANI_R$ across the three catchments, HD and LD had the highest and lowest TN, NO_3-N, and NH_4-N fluxes, respectively (Fig. 3).

Nitrate was the dominant form of N (51–69% of TN) for each catchment and its contribution to TN displayed increasing, steady, and decreasing trends in LD, MD, and HD from 1980 to 2010,

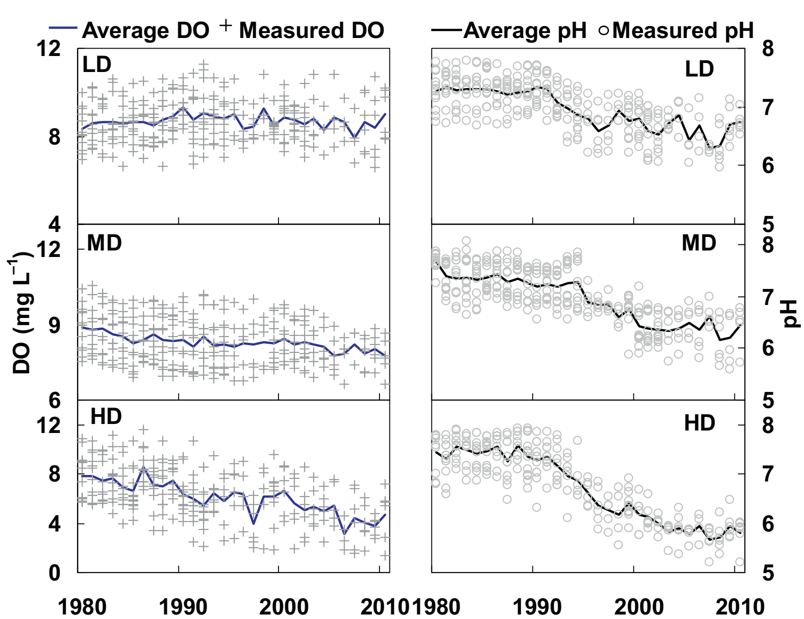

Fig. 4. Historical trends in measured and annual average riverine DO concentrations (left) and pH values (right) in the three catchments affected by low (LD), medium (MD), and high (HD) levels of anthropogenic disturbance in 1980–2010. Except for average DO concentration in catchment LD, trends for all others constituents between 1980 and 2010 were statistically significant ($p < 0.05$).

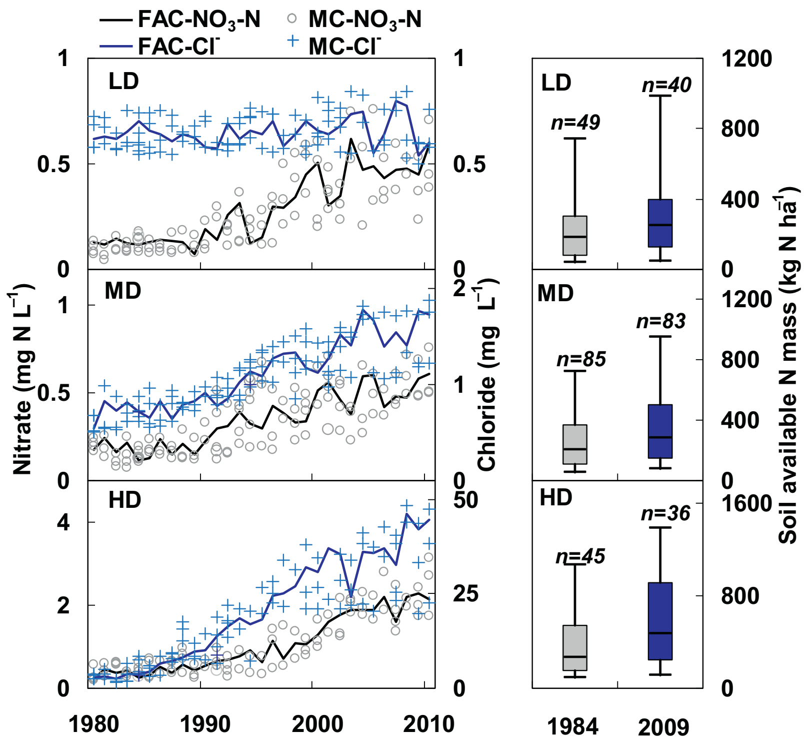

Fig. 5. Historical trends in measured (MC) and flow-adjusted (FAC) riverine nitrate and chloride (Cl^-) concentrations during the low flow regime (the lowest 30% of flow records) in 1980–2010 (left) and changes of available N levels in the upper 20-cm layer of agricultural soil between 1984 and 2009 (right) in the three catchments affected by low (LD), medium (MD), and high (HD) levels of anthropogenic disturbance. Except for Cl^- concentration in catchment LD, trends of all others constituents between 1980 and 2010 were statistically significant ($p < 0.01$). Measured available N level in soil between 1984 and 2009 in each catchment were significant difference ($p < 0.01$). Box plot denotes 97.5%, 75%, 50%, 25%, and 2.5% confidence of soil available N level.

respectively (Fig. 3). In comparison, NH_4-N contributed 9–33% of TN on average and its contribution increased in each catchment over the past 31 years. For HD, the contribution of NH_4-N exceeded that of NO_3-N since 2006. Catchments LD and HD had the lowest and highest proportion of NH_4-N to TN, respectively.

Over the 31-year study, the annual average dissolved oxygen (DO) concentration showed no significant change in LD ($p > 0.05$), whereas it significantly decreased by 13% and 40% in MD and HD, respectively (Fig. 4). River water pH decreased significantly in each catchment (~1.0 for LD, ~1.2 for MD, and ~1.6 for HD). Annual flow-adjusted average Cl^- concentration during the low flow regime showed no significant change in LD ($p > 0.05$), while it increased 0.5-fold and 8.8-fold between 1980 and 2010 in MD and HD, respectively (Fig. 5). Annual flow-adjusted average NO_3-N concentration during the low flow regime (Fig. 5) increased significantly in each catchment (~3.5-fold for LD, ~2.5-fold for MD, and ~2.2-fold for HD). There was an average 63, 84 and 204 kg N ha^{-1} net increase in available N (NH_4-N + NO_3-N) in the upper 20-cm layer of agricultural soils between 1984 and 2009 in catchments LD, MD and HD, respectively (Fig. 5), which is consistent with a 359, 615, and 1349 kg N ha^{-1} of cumulative $NANI_{FA}$ added to the agricultural/forest land (Fig. 2). On average, HD had the lowest DO concentration and highest Cl^- concentration and agricultural soil available N level, while catchment LD had the opposite trend.

3.3. Models linking catchment nitrogen budget and riverine nitrogen flux

In each catchment, annual riverine TN flux was significantly correlated with NANI, $NANI_{FA}$ and $NANI_R$, and their relationships were best described by an exponential function (Table 2). However, increasing trends in riverine TN, NO_3-N, and NH_4-N fluxes did not fully match changes in NANI as well as $NANI_{FA}$. Between 2000 and 2010, riverine N fluxes continuously increased in spite of a decline or no change in NANI or $NANI_{FA}$ (Figs. 2 and 3). The increasing TN flux was significantly related to the 58–65% increase in developed

Table 2
Best regressions between annual riverine TN flux (*F*, kg N ha^{-1} yr^{-1}) and NANI (kg N ha^{-1} yr^{-1}), NANI to forest/agricultural system ($NANI_{FA}$, kg N ha^{-1} yr^{-1}) and residential ($NANI_R$, kg N ha^{-1} yr^{-1}) lands, discharge (*Q*, $m^3 s^{-1}$), precipitation (*P*, mm yr^{-1}), developed land area percentage (D%) and percentage of agricultural lands with improved drainage (AD%) in the three catchments affected by low (LD), medium (MD), and high (HD) levels of anthropogenic disturbance in 1980–2010.

Catchment	Regressions	R^2	*n*
LD	$F = 0.036\exp(0.19NANI)$	0.88^{**}	31
	$F = 0.054\exp(0.26NANI_{FA})$	0.89^{**}	31
	$F = 0.048\exp(0.55NANI_R)$	0.70^{**}	31
	$F = 0.71Q^{0.47}$	0.17^{*}	31
	$F = 3.51P - 3.01$	0.21^{*}	31
	$F = 0.054AD\%^{1.42}$	0.31^{**}	31
	$F = 3.84D\%^{2.75}$	0.36^{**}	31
MD	$F = 0.42\exp(0.067NANI)$	0.86^{**}	31
	$F = 0.54\exp(0.090NANI_{FA})$	0.77^{**}	31
	$F = 0.53\exp(0.18NANI_R)$	0.76^{**}	31
	$F = 0.81Q^{0.60}$	0.21^{*}	31
	$F = 2.78P^{1.59}$	0.21^{*}	31
	$F = 0.38AD\%^{0.91}$	0.43^{**}	31
	$F = 2.41D\%^{1.61}$	0.37^{**}	31
HD	$F = 1.96\exp(0.019NANI)$	0.58^{**}	31
	$F = 3.96\exp(0.025NANI_{FA})$	0.26^{**}	31
	$F = 3.34\exp(0.032NANI_R)$	0.71^{**}	31
	$F = 13.67Q^{0.68}$	0.31^{**}	31
	$F = 8.05P^{1.45}$	0.31^{**}	31
	$F = 0.71AD\%^{0.84}$	0.35^{**}	31
	$F = 0.67D\%^{1.50}$	0.43^{**}	31

** $p < 0.01$.
* $p < 0.05$.

Table 3
Calibrated model Eq. (6) parameters for predicting riverine TN exports using an exponential function of NANI to forest/agricultural ($NANI_{FA}$) and residential ($NANI_R$) lands and a power function of discharge (Q, $m^3\,s^{-1}$), developed land area percentage (D%) and percentage of agricultural lands with improved drainage (AD%) in the three catchments affected by low (LD), medium (MD), and high (HD) levels of anthropogenic disturbance in 1980–2010.

Catchment	Parameters	Mean	95% CI	Std.	*P*
LD	α	0.0226	0.019–0.342	0.015	<0.001
	β_1	0.487	0.342–0.623	0.148	<0.001
	β_2	0.352	0.298–0.434	0.200	<0.001
	β_3	0.195	0.113–0.254	0.103	0.018
	β_4	2.072	1.673–2.423	0.576	<0.001
	β_5[a]	–			
	Calibrated model	$F = 0.0226Q^{0.487}[AD\%^{0.352}\exp(0.195NANI_{FA}) + D\%^{2.072}]$			
MD	α	0.029	0.022–0.034	0.012	<0.001
	β_1	0.503	0.342–0.665	0.079	<0.001
	β_2	0.532	0.362–0.674	0.179	<0.001
	β_3	0.070	0.590–0.820	0.010	<0.001
	β_4[a]	–			
	β_5	0.235	0.166–0.305	0.134	0.014
	Calibrated model	$F = 0.029Q^{0.503}[AD\%^{0.532}\exp(0.07NANI_{FA}) + \exp(0.235NANI_R)]$			
HD	α	0.319	0.276–0.341	0.101	<0.001
	β_1	0.617	0.500–0.734	0.157	<0.001
	β_2	0.549	0.476–0.631	0.132	<0.001
	β_3	0.020	0.015–0.026	0.006	<0.001
	β_4	0.746	0.589–0.895	0.118	<0.001
	β_5	0.038	0.029–0.048	0.016	<0.001
	Calibrated model	$F = 0.319Q^{0.617}[AD\%^{0.549}\exp(0.02NANI_{FA}) + D\%^{0.746}\exp(0.038NANI_R)]$			

[a] Parameter not significant at $p = 0.05$.

land area (Table 1) and a 96–108% increase in agricultural land area with improved drainage systems (Appendix B, Fig. B.1). Although no significant trends in precipitation or river discharge were observed over the study period ($p > 0.05$, Appendix A, Fig. A.1), annual riverine TN flux was positively correlated with precipitation and river discharge (Table 2).

Based on the analyses reported above as well as previous modeling efforts linking NANI and hydroclimate variables to riverine N export (McIsaac et al., 2001; Han et al., 2009; Chen et al., 2014a; Huang et al., 2014), we developed the following model linking $NANI_{FA}$ and $NANI_R$ to riverine TN flux (*F*, kg N $ha^{-1}\,yr^{-1}$) in each catchment:

$$F = \alpha Q^{\beta_1}\left[AD\%^{\beta_2}\exp(\beta_3 NANI_{FA}) + D\%^{\beta_4}\exp(\beta_5 NANI_R)\right] \quad (6)$$

where *Q* is annual average river discharge ($m^3\,s^{-1}$), D% is developed land area percentage, AD% is agricultural lands with improved drainage percentage, and α, β_1, β_2, β_3, β_4 and β_5 are fitting parameters.

Except for β_5 in catchment LD and β_4 in catchment MD, all other calibrated parameters were statistically significant ($p < 0.05$, Table 3). The non-significant parameters β_5 in catchment LD and β_4 in catchment MD imply that the influence of $NANI_R$ and D% on riverine TN flux in these catchments were negligible. The calibrated model (Eq. (6)) accounted for 93–97% of the variation in annual TN fluxes over the 31-year study period with Nash–Sutcliffe coefficients >0.92 between modeled TN flux and LOADEST-estimated values (Fig. 6). The mean relative error of prediction accuracy for individual years was <10% and the interquartile range for each year was relatively symmetrical, ranging from −24% to +24%.

3.4. Source apportionment of riverine nitrogen fluxes

Based on calibrated Eq. (6), annual riverine TN flux derived from current year's $NANI_{FA}$ (F_{FA}) and $NANI_R$ (F_R) in each catchment was determined:

$$F_{FA} = \alpha Q^{\beta_1} AD\%^{\beta_2}\left[\exp(\beta_3 NANI_{FA}) - 1\right] \quad (7)$$

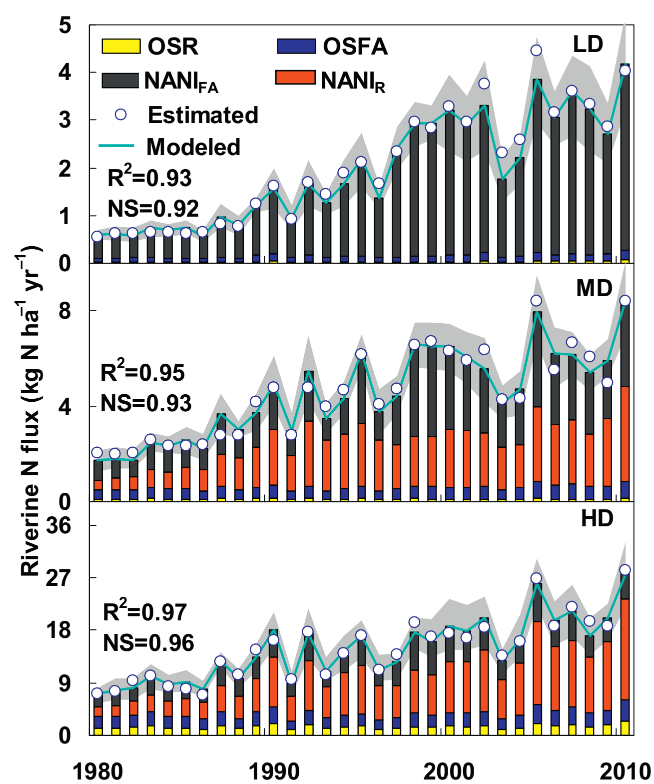

Fig. 6. LOADEST-estimated versus modeled riverine TN fluxes using model Eq. (6) and estimated contributions of current year $NANI_{FA}$, $NANI_R$, other sources in forest/agricultural (OSFA, e.g., natural background and legacy N sources) and residential lands (OSR, e.g., natural background, legacy, and industrial N sources) to annual riverine TN flux for the three catchments affected by low (LD), medium (MD), and high (HD) levels of anthropogenic disturbance in 1980–2010. Shadow area denotes the 95% confidence interval of the modeled TN fluxes. NS denotes Nash–Sutcliffe coefficient.

$$F_R = \alpha Q^{\beta_1} D\%^{\beta_4}[\exp(\beta_5 NANI_R) - 1] \quad (8)$$

Referring to methods for estimating natural background sources (e.g., natural vegetation biological N fixation, rock release) to riverine N fluxes in previous studies (Han et al., 2009; Howarth et al., 2012; Swaney et al., 2012), this study assumed that the component of riverine N flux that was not explained by current year's $NANI_{FA}$ and $NANI_R$ in Eq. (6) was derived from N sources not incorporated into the NANI budgets. These other sources contributing to the riverine N flux in the forest/agricultural system (e.g., natural background and legacy sources, F_{OSFA}) and residential system (e.g., natural background and legacy sources, and industrial sewage, F_{OSR}) were estimated as follows:

$$F_{OSFA} = \alpha Q^{\beta_1} AD\%^{\beta_2} \quad (9)$$

$$F_{OSR} = \alpha Q^{\beta_1} D\%^{\beta_4} \quad (10)$$

Over the 1980–2010 period, the estimated current year's $NANI_{FA}$ contribution to riverine TN export was (kg N ha^{-1} yr^{-1}): LD = 1.8 (90%), MD = 2.1 (44%), and HD = 4.0 (27%) on average (Fig. 6). In comparison, current year's $NANI_R$ contributions to riverine TN exports followed (kg N ha^{-1} yr^{-1}): LD = 0 (0%), MD = 1.9 (41%), and HD = 7.0 (45%). With the exception of $NANI_R$ in LD, annual riverine TN flux derived from current year's $NANI_{FA}$ or $NANI_R$ presented a significant increasing trend ($p < 0.01$) over time. The natural background (i.e., forest and natural vegetation biological N fixation or rock N release) and legacy N sources (i.e., surplus N stored in watershed soils and groundwater that is derived from anthropogenic N inputs in previous years, Chen et al., 2014b) in the forest/agricultural system contributed 8%, 12%, and 17% of annual riverine TN fluxes on average for LD, MD, and HD, respectively. The natural background (i.e., natural vegetation biological N fixation or rock N release), legacy, and industrial (i.e., industrial sewage discharge) N sources in residential systems contributed 2%, 3%, and 11% for LD, MD, and HD, respectively. Overall, natural background, legacy, and industrial N source contribution to annual riverine TN fluxes followed (kg N ha^{-1} yr^{-1}): LD = 0.2 (10%), MD = 0.6 (15%), and HD = 3.8 (28%) (Fig. 6). Annual riverine TN flux derived from these N sources displayed an increasing trend ($p < 0.01$) with time in all three catchments. Of cumulative riverine TN flux, 98%, 56% and 42% were derived from the forest/agricultural system, while 2%, 44% and 58% originated from the residential system for LD, MD, and HD, respectively.

4. Discussion

4.1. Efficacy and implications of the N budget-riverine TN flux model

The developed model (Eq. (6)) incorporating $NANI_{FA}$, $NANI_R$, land use and discharge provided highly accurate predictions for riverine TN fluxes (Fig. 6), similar to models developed for other watersheds (McIsaac et al., 2001; Han et al., 2009; Gao et al., 2014; Chen et al., 2014a; Huang et al., 2014). Beyond the scope of other models was the ability to quantify the individual contributions of $NANI_{FA}$, $NANI_R$, and other sources (e.g., natural background, legacy, and industrial N sources) to riverine TN flux. Estimated results indicated that $NANI_R$ has no significant contribution to riverine TN flux in catchment LD, while the $NANI_R$-contributed N flux increased rapidly in the catchments more strongly impacted by anthropogenic activities (MD and HD) (Fig. 6). These results are supported by the lack of a significant increase for Cl^- (a conservative indicator for sewage, Jarvie et al., 2012) during the low flow regime (no runoff input and limited dilution effect) and lack of a significant decrease for DO concentration ($p > 0.05$) in LD (Fig. 4 and Fig. 5). In contrast, significant increasing trend for Cl^- and decreasing trend for DO ($p < 0.05$) were observed in MD and HD over the study period. Spatially, residential systems in LD, MD, and HD exported low, median, and high N fluxes, respectively (Fig. 3), which is consistent with spatial distributions of Cl^- and DO concentrations across all three catchments (Fig. 5). These comparisons support the efficacy and robustness of the model for quantifying the sources of riverine TN fluxes.

The model results indicated that N fluxes from other sources in the forest/agricultural system were far larger than those in the residential system (Fig. 6), implying that industrial N sources have a limited contribution to riverine TN fluxes. Considering the similar soil attributes and precipitation amounts among the three catchments (Table 1), we further assumed that the estimated annual N flux derived from other sources in the residential system of LD was from natural background sources. As a result, ~14%, ~11%, and ~12% of cumulative $NANI_{FA}$ and 0%, ~17%, and ~20% of cumulative $NANI_R$ over the past 31 years were estimated to be exported via rivers from LD, MD, and HD, respectively. This highlights the importance of independently examining the $NANI_{FA}$ and $NANI_R$ components to identify their individual contributions to riverine N flux, further indicating the usefulness of the developed model. Of the cumulative NANI, ~10%, ~13% and ~16% were exported by rivers in LD, MD and HD, respectively. These estimates fall within the range reported (5–40%) in previous studies in America, Europe and China (Sobota et al., 2009; Swaney et al., 2012; Howarth et al., 2012; Gao et al., 2014). Differences in estimated NANI export fractions among the three catchments were consistent with the spatial distribution of $NANI_R$ contribution to NANI (Fig. 2) and the percentages of developed land area and agricultural lands with improved drainage (Table 1).

The exponential relationship in Eq. (6) indicates that small changes in $NANI_{FA}$ and $NANI_R$ lead to relatively large changes in riverine TN flux due to progressive N saturation (i.e., N inputs exceeding N assimilative capacity by plants and microbes in terrestrial and aquatic ecosystems, McIsaac et al., 2001; Swaney et al., 2012). Progressive N saturation is supported by a decrease in river water pH since the 1990s (Fig. 4), especially in LD having the highest forest percentage (Table 1). Due to increasing NO_3^- leaching from progressive N saturation, the greater affinity of protons for cation exchange sites in the soil will displace base cations. As base cation saturation is decreased, increased leaching of protons or mobilized aluminum with ensue leading to stream water acidification (Fang et al., 2011; Nakahara et al., 2010). In temperate catchments as well as in subtropical forests of southern China, ~10.7 kg N ha^{-1} yr^{-1} of anthropogenic N input has been suggested as an N-saturation threshold (Howarth et al., 2012; Swaney et al., 2012; Zhang et al., 2013). This implies that atmospheric N inputs to forests in our study region (NH_4-N + NO_3-N = 25.0 – 35.0 kg N ha^{-1} yr^{-1}, Appendix D) have likely contributed to progressive N saturation since the 1980s.

It should be pointed out that Eq. (6) model, which is supported by the observed relationships between riverine TN flux and each of the relevant influencing factors for the three catchments (Table 2), might be widely applicable for other watersheds. However, the influencing factors and function types in Eq. (6) may change and require optimization for application in different watersheds. Furthermore, caution should be given to potential uncertainties incorporated into the model results due to the lack of complete validation data for N fluxes derived from various sources as mentioned in Fig. 6 (it is very difficult to directly measure specific N sources at the catchment scale). Extensive watershed information, such as changes in soil, groundwater, and river N characteristics, other chemical properties, and human activities, is needed to further verify the model results.

4.2. Influence of nitrogen sources and land use on riverine nitrogen export

For the three catchments, NANI and riverine TN exports presented contrasting trends (i.e., NANI decreased or remained steady while riverine N export increased) over the 2000–2010 period (Figs. 2 and 3). Although $NANI_{FA}$ decreased or remained steady since 2000, its contribution to riverine N flux increased in each catchment (Fig. 6). These results emphasize the importance of changes in NANI components ($NANI_{FA}$ vs $NANI_{R}$) and land use as well as legacy N sources/progressive N saturation in regulating riverine N exports. For LD, such contrasting trends between 2000 and 2010 resulted mainly from increasing $NANI_{FA}$-contributed N flux due to progressive N saturation from atmospheric deposition and a 75% increase in agricultural land area with improved drainage (Appendix B, Fig. B1), since $NANI_{R}$ (0%) and legacy N sources (~8%) had a limited contribution to riverine N flux (Fig. 6). Improved agricultural land drainage increased the $NANI_{FA}$ export fraction since it improves hydrologic connectivity and enhances N delivery from land to river by decreasing the residence time for N retention processes (McIsaac and Hu, 2004; Kopáček et al., 2013; Chen et al., 2014b).

The continuous increase in riverine N export in MD over the 2000–2010 period is likely due to increased N fluxes derived from both $NANI_{FA}$ and $NANI_{R}$ as well as forest/agricultural legacy sources (Fig. 6). Since $NANI_{FA}$ decreased in 2000–2010, the increased $NANI_{FA}$-contributed N flux resulted from a higher $NANI_{FA}$ export fraction associated with the 80% increase of agricultural lands with improved drainage (Appendix B, Fig. B1). Improved drainage efficiency would also increase the forest/agricultural legacy N contribution. This is supported by the 84 kg N ha^{-1} increase of available soil N between 1984 and 2009 in the upper 20-cm layer of agricultural soils (also implying N enrichment in deeper soils) and a ~2.5-fold increase in flow-adjusted nitrate concentrations during the low flow regime (i.e., groundwater inputs) between 2000 and 2010 (Fig. 5). Both soil available N and groundwater nitrate enrichment are likely associated with improved agricultural drainage efficiency. In addition, increased soil aeration results in lower N immobilization and higher mineralization of soil organic matter, leading to nitrate enrichment in soils and enhancing nitrate leaching to deeper soil horizons, groundwater and rivers (Kopáček et al., 2013; Chen et al., 2014b). This hypothesis was supported by a 12.4% decrease in soil organic matter between 1984 and 2009 observed in the upper Jiaojiang watershed (Chen et al., 2014a). Given a relatively steady $NANI_{R}$ in 2000–2010, the increased $NANI_{R}$-contributed N flux mainly results from an increase in the $NANI_{R}$ export fraction due to increased direct discharge of domestic and animal waste into rivers and expanding developed land area (Table 1). As a result, there was a ~53% increase in Cl^{-} concentration (Fig. 5) and a 44% increase in NH_4-N flux (Fig. 3) in 2000–2010. Increasing developed land area (more impervious surface areas) also decreases retention capacity and enhances flushing of N originating from untreated domestic and animal wastes in residential systems (Appendix D, Table D.2) during rainfall events due to an increased runoff-to-infiltration ratio (Groffman et al., 2004; Kaushal et al., 2008).

For HD, the continuous increase in riverine N export over the 2000–2010 period mainly resulted from increased N fluxes derived from $NANI_{FA}$, $NANI_{R}$, and legacy sources (Fig. 6). Increasing $NANI_{R}$-contributed N flux is associated with increasing $NANI_{R}$ (Fig. 2) as well as an enhanced $NANI_{R}$ export fraction. Direct discharge of sewage in HD is believed to be considerably higher than MD as supported by a larger decrease in DO concentration (Fig. 4) and a higher increase in Cl^{-} concentration during the low flow regime between 2000 and 2010 (Fig. 5). As a result, the riverine NH_4-N flux increased 90% and NH_4 became the dominant N form since 2006 (Fig. 2). A significant decrease of DO concentration coupled with a rapid decrease in pH (Fig. 4) may reduce in-stream nitrification of NH_4 to NO_3 (Dai et al., 2008; Vogt et al., 2015), further contributing to the dominance of NH_4 in HD since 2006. Given higher percentages of agricultural lands with improved drainage and developed lands (Table 1) and greater N enrichment in agricultural soils and groundwater (Fig. 5), export fractions for $NANI_{FA}$, $NANI_{R}$ and legacy sources are higher in HD than MD (Fig. 6). This is supported by higher runoff coefficients in HD compared to catchments LD and MD (Table 1).

4.3. Fate of surplus nitrogen

For cumulative NANI in the three catchments between 1980 and 2010, 10–16% was exported by rivers. The remaining 84–90% of NANI was stored in non-harvested biomass, soils and groundwater, and removed by denitrification (Yan et al., 2011; Chen et al., 2014a). A previous study estimated that ~25% of total NANI was stored in soils and groundwater for this region (Chen et al., 2014b). Nitrogen storage in soils was supported by significant increase in available N observed in the agricultural upper 20-cm layer soils between 1984 and 2009 in each catchment (Fig. 5). Similar results were observed in the 0–400 cm depth of soil profiles in several agricultural soils of China with 209–1776 kg N ha^{-1} of nitrate accumulation after 3–16 years of N fertilizer application (110–900 kg N ha^{-1} yr^{-1}) (Ju et al., 2004). Accumulation of N in groundwater was indicated by the 2.2~3.5-fold increase of flow-adjusted nitrate concentrations during the low flow regime (Fig. 5). Field experiments in nearby regions also indicated that 3.4% and 11.1% of annual N fertilizer applied to rice and upland crops was lost via deep leaching, respectively (Ti et al., 2012). Additionally, ponds and wetlands in a nearby region retained 83 kg N ha^{-1} yr^{-1} within soils, vegetation and plant litter (Yan et al., 2011).

Considering the high percentage of forest cover (>45%) in the three catchments, forest biomass uptake is another likely N sink. If we assume that forest biomass retains ~34% of atmospheric N deposition (NH_4-N + NO_3-N) as observed in eastern China (Sheng et al., 2014), 16%, 8%, and 3% of NANI may be retained in the forest biomass of LD, MD, and HD, respectively. This is supported by a ~60% increase in foliar N content in unfertilized non-agricultural ecosystems in eastern China between 1980 and 2010 (Liu et al., 2013).

Based on the estimates above, denitrification would by difference account for the fate of 49%, 54%, and 57% of total NANI in LD, MD, and HD, respectively. These denitrification percentages are comparable to the sum of field denitrification (25–48% of N applied, Yan et al., 2011; Ti et al., 2012; Hofmeier et al., 2015; Gu et al., 2015) and in-stream denitrification (10–35% of N input to rivers, Yan et al., 2011; Chen et al., 2013) reported in the surrounding region. The higher denitrification percentage in HD may be due to lower river discharge and/or lower DO concentrations (Table 1 and Fig. 5), since in-stream denitrification is enhanced at smaller channel sizes (increased wetted surface area per unit water volume and decreased hydrologic residence time) and by anaerobic conditions (Chen et al., 2013).

4.4. Implications for catchment nitrogen management

Given the relative contributions to riverine TN fluxes (Fig. 6), reduction of $NANI_{FA}$ in LD and $NANI_{R}$ in HD will have the greatest impact on reducing riverine TN fluxes, while MD should consider both $NANI_{FA}$ and $NANI_{R}$ reductions. To reduce $NANI_{FA}$, decreasing chemical fertilizer application should be a primary target for all three catchments. For the three catchments, N fertilizer (chemical + manure) use efficiency ranges from 30–40%, which is consistent with results from nearby regions (Chen et al., 2009;

Xiao et al., 2015; Hofmeier et al., 2015). Therefore, a considerable reduction of current chemical fertilizer application rate (Fig. D.4) would likely have little influence on crop yield while substantially decreasing riverine TN export. In some regions of China, decreased recycling of human and animal excreta over the past several decades (Wang et al., 2011; Gu et al., 2015) and the lack of efficient sewage collection and treatment (Chen et al., 2013) have been major causes for increased nutrient pollution. To reduce $NANI_R$, it would be advantageous to promote recycling of human and domestic animal wastes to partially replace chemical fertilizer use on croplands. Furthermore, targeting human and domestic animal wastes serves a critical issue of reducing NH_4-N concentration and hypoxia in surface waters, which pose big risks for downstream aquatic ecosystems, especially in HD.

Model results (Table 3) suggest that changes in land use and climate (e.g., increasing precipitation or river water discharge in future) can amplify riverine N export via enhancing N delivery efficiency from catchment landscapes to rivers. Furthermore, legacy anthropogenic N transiently stored in soil and groundwater (Fig. 5) has the potential to increase N flux with future changes in climate and land use. Therefore, the influence of climate and land-use changes should be considered as part of management efforts to control N water pollution (Huang et al., 2014). Given the enhanced N delivery efficiency by future climate and land-use changes, it is advantageous to adopt and improve N interception measures along the hydrologic flowpath using constructed ecological ditches, flow-through wetlands, and riparian buffer strips to mitigate N export from agricultural and residential lands (Billen et al., 2009; Chen et al., 2013).

5. Conclusion

This study highlights the importance of changes in NANI magnitude and components ($NANI_{FA}$ vs $NANI_R$), hydroclimate, land use, and legacy N sources in controlling long-term changes of riverine TN export. For the three catchments examined in this study, riverine TN flux continuously increased 3.0 ~ 6.1-fold between 1980 and 2010. These changes resulted from increasing NANI (especially $NANI_R$) and increasing fractional delivery of NANI and legacy N enhanced by increasing developed land area, improved agricultural drainage efficiency, and progressive N saturation. The model developed in this study incorporates these influencing factors and provides a simple and effective method for predicting and indentifying the TN fluxes derived from forest/agricultural and residential systems in each catchment. Models estimated $NANI_{FA}$, $NANI_R$ and other N sources (e.g., natural background, legacy, and industrial N sources) contributed 27–90%, 0–45%, and 10–28% of annual riverine TN fluxes, respectively. Model results were consistent with expected spatio-temporal variations of riverine chloride, ammonium, nitrate, dissolve oxygen and pH, as well as changes in available N levels in agricultural soils and groundwater. In terms of N source management, reduction of $NANI_{FA}$ in catchment LD and $NANI_R$ in catchment HD would have the greatest impact on reducing riverine TN fluxes. Changes in anthropogenic N input components ($NANI_{FA}$ vs $NANI_R$) and land-use/climate as well as legacy N sources can amplify riverine N export and should be considered in developing N management strategies.

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Appendix A. Supplementary data

A: Long-term changes of annual precipitation and water discharge; B: Soil characteristics and management; C: LOADEST model for riverine N flux estimation; D: Estimation of forest/agricultural and residential N budgets and uncertainty analyses.

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.agee.2016.01.037.

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