## Title

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## Authors

Huang, Hong
Chen, Dingjiang
Zhang, Baifa
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# Modeling and forecasting riverine dissolved inorganic nitrogen export using anthropogenic nitrogen inputs, hydroclimate, and land-use change

Hong Huang [a,b], Dingjiang Chen [a,c,*], Baifa Zhang [a], Lingzao Zeng [a], Randy A. Dahlgren [d]

[a] College of Environmental Science and Resources, Zhejiang University, Hangzhou 310058, China
[b] Zhejiang Provincial Key Laboratory of Subtropical Soil and Plant Nutrition, Zhejiang University, Hangzhou 310058, China
[c] Ministry of Education Key Laboratory of Environment Remediation and Ecological Health, Zhejiang University, Hangzhou 310058, China
[d] Department of Land, Air, and Water Resources, University of California, Davis, CA 95616, USA

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SUMMARY

A quantitative understanding of riverine nitrogen (N) export in response to human activities and climate change is critical for developing effective watershed N pollution control measures. This study quantified net anthropogenic N inputs (NANI) and riverine dissolved inorganic N (DIN = $NO_3$–N + $NH_4$–N + $NO_2$–N) export for the upper Jiaojiang River catchment in eastern China over the 1980–2010 time period and examined how NANI, hydroclimate, and land-use practices influenced riverine DIN export. Over the 31-yr study period, riverine DIN yield increased by 1.6-fold, which mainly results from a ~77% increase in NANI and increasing fractional delivery of NANI due to a ~55% increase in developed land area. An empirical model that utilizes an exponential function of NANI and a power function of combining annual water discharge and developed land area percentage could account for 89% of the variation in annual riverine DIN yields in 1980–2010. Applying this model, annual NANI, catchment storage, and natural background sources were estimated to contribute 57%, 22%, and 21%, respectively, of annual riverine DIN exports on average. Forecasting based on a likely future climate change scenario predicted a 19.6% increase in riverine DIN yield by 2030 due to a 4% increase in annual discharge with no changes in NANI and land-use compared to the 2000–2010 baseline condition. Anthropogenic activities have increased both the N inputs available for export and the fractional export of N inputs, while climate change can further enhance riverine N export. An integrated N management strategy that considers the influence of anthropogenic N inputs, land-use and climate change is required to effectively control N inputs to coastal areas.



## 1. Introduction

Excessive nitrogen (N) in rivers from anthropogenic activities is of increasing concern worldwide as it degrades aquatic ecosystem health, decreases water quality for beneficial uses, and causes eutrophication and hypoxia in many coastal ecosystems (Edwards and Withers, 2008; Howden et al., 2011; Howarth et al., 2012; Chen et al., 2013). The extent of riverine N export is dependent on various factors, such as anthropogenic N inputs (Howarth, 2008), hydroclimate (McIsaac et al., 2001; Han et al., 2009), and land-use/land-management practices (Groffman et al., 2004; Kaushal et al., 2008; Sobota et al., 2009). Therefore, to effectively guide N management for protecting aquatic ecosystem health, models that predict riverine N export must be responsive to changes in these factors.

Net anthropogenic nitrogen input (NANI) is a nitrogen-budgeting approach that sums N contributions from atmospheric deposition, fertilizer application, agricultural biological fixation, and net import/export of N in food, feed and seed to a watershed (Howarth et al., 2012; Han et al., 2014). NANI has been widely recognized as an effective tool to explain among-watershed or among-year variations of riverine N fluxes (McIsaac et al., 2001; Howarth, 2008; Howarth et al., 2012; Han et al., 2009). Although the relationship between NANI and riverine N export is generally strong, such a relationship is additionally influenced by variations in hydroclimate and land-use (Han et al., 2009; Sobota et al., 2009; Howden et al., 2010). It is commonly observed that years with higher precipitation or discharge exported a higher fraction of NANI by rivers, whereas drier years exported a lower fraction of NANI (Howarth, 2008; Han et al., 2009; Schaefer et al., 2009).

* Corresponding author. Permanent address: College of Environmental Science and Natural Resources, Zhejiang University, 866# YuHangTang Road, Hangzhou 310058, Zhejiang Province, China. Tel./fax: +86 571 88982071.
*E-mail address:* chendj@zju.edu.cn (D. Chen).

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Therefore combining the influence of NANI with either precipitation or discharge can generally explain the variability in mean N flux among watersheds or years with a higher accuracy (Howarth et al., 2006; Han et al., 2009; Swaney et al., 2012). Furthermore, fractional export of NANI by rivers varies with land-use, with higher factional export generally observed in urban or suburban watersheds than in agricultural or forest watersheds, due to increased impervious surfaces and reduced hydrologic residence times that reduce retention capacity during N transport (Groffman et al., 2004; Kaushal et al., 2008; Elmore and Kaushal, 2008). However, based on our review of the literature there is a paucity of studies that simultaneously considered the influence of NANI, hydroclimate, and land-use on riverine N exports. Such an integrated approach is required for watersheds or regions that have experienced extensive changes in land-use/land-cover, climate and/or agricultural practices over time.

A number of studies indicated that 10–40% of multi-year averaged NANI was exported by rivers (Howarth et al., 2012; Swaney et al., 2012), implying that a considerable proportion of NANI was temporally stored in aquifers, soils and/or biomass (~27%), although a higher proportion was attributed to denitrification (~57%) (Van Breemen et al., 2002). These stored N sources, which are not addressed by the NANI budget approach (Swaney et al., 2012), have the potential to release N to rivers in following years (Stålnacke et al., 2003). For example, studies have shown that 25–40% of the annual riverine N loss may originate from the mineralization of soil organic N (Booth et al., 2005; Kopáček et al., 2013) and nitrate exported from groundwater could account for 35–40% of the riverine N flux (Iqbal, 2002; Lindsey et al., 2003). In the Mississippi River, annual riverine nitrate flux was determined by NANI to the watershed from the previous 2–9 yr (McIsaac et al., 2001). However, limited knowledge is available on what proportion of riverine N export in a given year or period is derived from the storage of NANI from previous years. Such information is critical to better understand how watershed N sinks and riverine N exports change in response to changes in NANI and land-use, as well as climate change over extended time periods (Swaney et al., 2012).

Since the 1980s, Chinese rivers, such as the Yangzi River, Yellow River and Zhujiang River, have experienced a significant increase in N concentration and flux associated with rapid economic development, human population expansion, and urbanization (Duan et al., 2000; Xia et al., 2002; Liu et al., 2003; Li et al., 2007; Shen and Liu, 2009). Due to the lack of long-term river N monitoring records, historical N trend analyses have been limited to these major rivers, while little information is available for smaller rivers, which may experience appreciably different N source-sink dynamics. Examining trends in riverine N flux in response to changes in N inputs and land-use is especially important for watersheds in eastern China that have experienced the most rapid economic and society development in China since the 1980s. For these coastal waters along the East China Sea, excessive dissolved inorganic N (i.e., DIN = $NO_3$–N + $NH_4$–N + $NO_2$–N, which is the most bioavailable form of N) from coastal rivers has resulted in serious algal blooms and persistent hypoxia (Duan et al., 2000; Li et al., 2007; Gao and Zhang, 2010). Furthermore, although the relationship between NANI and riverine N export has been widely examined in American and European watersheds, few attempts have been conducted for Chinese watersheds. Accordingly, it is urgent to update and expand the quantitative knowledge of long-term riverine DIN trends in response to changes in NANI and land use over the past several decades for watersheds in eastern China to support the development of efficient coastal N pollution control strategies.

This study investigated a 31-yr record (1980–2010) of riverine DIN exports in response to changes in NANI, hydroclimate, and land use in the upper Jiaojiang catchment (2474 km$^2$) in eastern China; the third largest river of Zhejiang Province that ultimately flows into the East China Sea. The study is based on detailed data from long-term monitoring of riverine $NH_4$–N, $NO_3$–N, and $NO_2$–N concentrations and discharge, land-use, precipitation, and anthropogenic N sources. The primary objectives of this study were to (i) develop an empirical model of river DIN export that simultaneously incorporates the influences of NANI, hydroclimate, and land use, (ii) use the model to identify individual contribution from NANI, watershed N storage, and background sources to riverine DIN export, and (iii) predict future (2011–2030) trends in riverine DIN export based on scenarios for future changes in NANI, land use and climate. This study will inform development of N management strategies to effectively control N inputs to coastal waters experiencing persistent eutrophication and hypoxia.

## 2. Materials and methods

### 2.1. Watershed description

The upper Jiaojiang catchment (120° 13′ 46.065″–121° 0′ 52.464″E and 28° 28′ 10.118″–29° 2′ 22.156″N; elevation ~15–1000 m) is located in the highly developed Taizhou City area of Zhejiang Province, China (Fig. 1). The Jiaojiang River 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 (Duan et al., 2000; Li et al., 2007; Gao and Zhang, 2010). 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 an average annual temperature of 17.4 °C and average annual precipitation of 1400 mm (Fig. 2a). The rainfall mainly occurs in May–September with a typhoon season occurring in July–September. Agricultural land (including paddy field, garden plot, and dryland) averaged ~12% of total watershed area in 1980–2010, with developed land (including rural and urban residential lands, roads, and mining and industry lands) and woodland, and barren land (including water surface, swamp, rock, and natural reservation land) contributing ~3%, ~67%, and ~18%, respectively. Developed land area was increased by ~55% since 1980 (Fig. 2b). The economic role of agriculture has been increasingly replaced by industry since the 1990s, resulting in a large reduction in chemical N fertilizer application (~40%) and cultivated crop area (~20%) since 2000 (Fig. 2b). Total population within the catchment increased from ~590,000 in 1980 to ~740,000 in 2010. Over the 31-yr study period, domestic livestock production (pig, cow, sheep, and rabbit) decreased by ~25%, poultry production (chicken and duck) increased by 4.8-fold (Fig. 2c), and freshwater aquatic species production (fish and shrimp) increased by 11.7-fold.

### 2.2. Riverine DIN flux estimate

River water samples were collected once every 4–8 weeks ($n$ = 300 sampling times total) at Baizhiao station from 1980 to 2010 (Fig. 1) by the Taizhou City Environment Protection Bureau. A well-mixed composite water sample (surface and bottom layers at three sites along the cross section) was collected between 8:00 and 9:00 on each sampling date, and nitrogen forms were analyzed by the Taizhou City Environment Protection Bureau. Duplicate samples from the composite sample were acidified with $H_2SO_4$ in the field (10 ml of concentrated $H_2SO_4$ per liter) and filtered and analyzed within 4 h of sampling. The concentration of $NO_3^-$ in water sample was determined by the spectrophotometric phenol disulfonic acid method (limit of detection: LOD = 0.01 mg N L$^{-1}$);

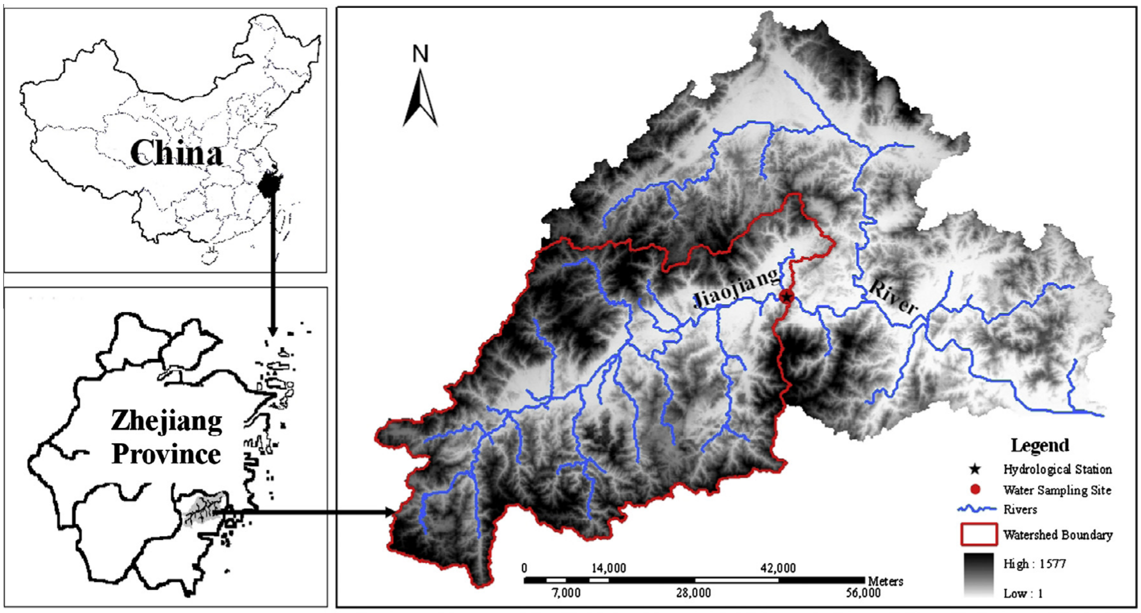


**Fig. 1.** Location of the upper Jiaojiang River in Zhejiang Province and its water quality and hydrology monitoring stations.

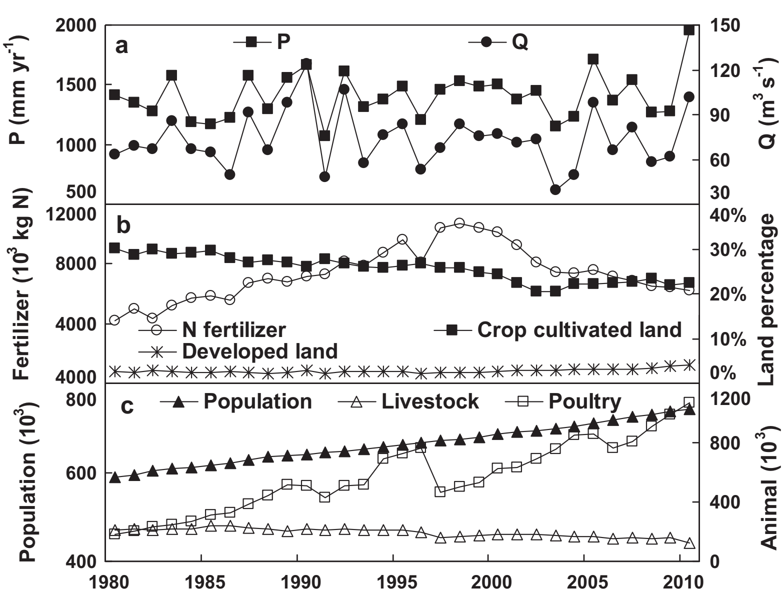


**Fig. 2.** Historical trends for precipitation ($P$) and river discharge ($Q$) (a), agricultural practices and developed lands (b), and population and domestic animal breeding (c) in the upper Jiaojiang watershed over the 1980–2010 period.

$NH_4^+$ by the spectrophotometric salicylic acid method (LOD = 0.02 mg N $L^{-1}$); and $NO_2^-$ by the spectrophotometric naphthyl ethylenediamine method (LOD = 0.003 mg N $L^{-1}$) (Duan et al., 2000). For samples with concentrations below the detection limit, concentrations were set at their respective detection limits for statistical analysis and modeling purposes. Data for daily river discharge at Baizhiao station (Fig. 1) and daily precipitation at three weather monitoring stations within the catchment were obtained from the Taizhou City Hydrology Bureau and Weather Bureau, respectively.

To estimate annual DIN flux using the discrete monitoring datasets for $NH_4$–N, $NO_3$–N, and $NO_2$–N concentrations in 1980–2010, the widely applied LOADEST model was utilized (Runkel et al., 2004):

$$Ln(L_t) = \beta_0 + \beta_1 Ln(Q_t) + \beta_2 Ln(Q_t)^2 + \beta_3 t + \beta_4 t_c^2 + \beta_5 \sin(2\pi t) + \beta_6 \cos(2\pi t) \quad (1)$$

where $Ln$ is the natural logarithm function; $Q_t$ is daily average river discharge for a given N monitoring date ($m^3\ s^{-1}$), $L_t$ is the measured daily N flux (kg N $d^{-1}$), which is estimated by multiplying measured N concentration by $Q_t$; $t$ is the decimal time for the corresponding monitoring date; $t_c$ is the center of decimal time for the study period (a constant); $\beta_0 \cdots \beta_6$ are the fitted parameters in the multiple regression; $\beta_1$ and $\beta_2$ describe the relation between flux and discharge; $\beta_3$ and $\beta_4$ describe the relationship between flux and time; and $\beta_5$ and $\beta_6$ describe seasonal variation in flux data.

In this study, the LOADEST model was developed for daily $NH_4$–N, $NO_3$–N, and $NO_2$–N fluxes, respectively. The unknown parameters (i.e., $\beta_0 \cdots \beta_6$) were optimized by Akaike information criterion and Schwarz criteria (Posada and Buckley, 2004) for various LOADEST formats using EViews software (version 6, Quantitative Micro Software Inc., USA, 2002). The regression $R^2$, Nash–Sutcliffe efficiency (Chen et al., 2013), and Durbin-Watson statistic (Alkorta et al., 2000) were adopted to assess the performance of the LOADEST models. Daily $NH_4$–N, $NO_3$–N, and $NO_2$–N fluxes for non-monitoring dates were estimated using the daily $Q$ and $t$ by the calibrated LOADEST model. Annual $NH_4$–N, $NO_3$–N, and $NO_2$–N fluxes were estimated as the sum of the daily fluxes for a corresponding year, and annual DIN yield (kg N $ha^{-1}$ $yr^{-1}$) and average DIN concentration (mg N $L^{-1}$) were determined by dividing annual DIN flux (the sum of annual $NH_4$–N, $NO_3$–N, and $NO_2$–N fluxes) by the total catchment area and annual cumulative river water discharge, respectively.

### 2.3. NANI calculation and uncertainty analysis

NANI was calculated as the sum of five major components: atmospheric N deposition, fertilizer N application, agricultural N fixation, seed N input, and net N import/export in food and feed. The net N food and feed balance was composed of crop and livestock production and N consumption by livestock and humans (Han et al., 2011, 2014; Hong et al., 2013). Data sources for estimating the annual NANI budget for the upper Jiaojiang catchment from 1980 to 2010 were derived from the annual Statistic Yearbook for Xianju County and Linhai City. By defining the catchment boundary using a geographic information system (GIS), total annual anthropogenic N sources and sinks for the upper Jiaojiang catchment were summarized for Xianju County (~73% of total catchment area) and three towns within Linhai City (~12% of total catchment area). The remaining ~15% of the catchment area only considered the N input from atmospheric deposition in the NANI analysis, since it was dominated by forests (~95%) and fell within Panan County (located in the northwest portion of the catchment) and Jinyun County (located in the southwest portion of the catchment) (Fig. 1).

#### 2.3.1. Fertilizer N application

Annual chemical fertilizer N input was directly determined from the applied amount of each fertilizer type and corresponding N content. Annual statistics for the different types of nitrogen fertilizer, such as ammonium nitrate, ammonium bicarbonate, urea, and miscellaneous forms, were directly available from the yearbooks (Fig. 2b). The N content in urea, ammonium nitrate, ammonium bicarbonate, and other combined fertilizers were 46%, 35%, 17%, and 12.8%, respectively (Han et al., 2014).

#### 2.3.2. Atmospheric N deposition

Atmospheric N deposition was obtained from annual average N deposition values reported for southeast China in 1980–2010 by Liu et al. (2013) and for Zhejiang Province in 1981–2009 by Han et al. (2014). The only atmospheric input considered is $NO_y$ deposition originating largely from fossil-fuel combustion, which is considered a new input of N to the watershed (Han et al., 2014). Atmospheric N deposition did not include ammonia, given that most of the ammonia in the atmosphere is deposited near the site of emission, such as from agricultural or livestock sources already included in NANI.

#### 2.3.3. Agricultural biological N fixation

Agricultural N fixation associated with green manure, other leguminous plants, paddy fields, uplands, and garden plots was estimated based on the size of harvested area multiplied by average values for N fixed per unit area. The average N fixation rates were taken from relevant studies conducted near the Jiaojiang watershed (Table 1; Yan et al., 2011; Ti et al., 2012).

#### 2.3.4. Seed N input

In this study, we adopted the modification of Han et al. (2014) that takes the N content of seed as an input in the NANI estimate for China. Vegetables and the six main agricultural crops, which are the major agricultural plants in this study catchment, were considered to estimate seed N input. Seed N per unit area for each crop type was adopted from Han et al. (2014) (Table 1). Seed N input was estimated by multiplying the seed N input per unit area for each crop type by the cultivated area in the catchment.

#### 2.3.5. Net N import/export in food and feed

Net N import/export in food and feed was calculated as the sum of human N consumption and domestic animal N consumption, minus the sum of domestic animal and crop N production exported from the catchment. Human consumption of N in food was estimated by multiplying the number of inhabitants (Fig. 2c) by a per capita intake of N. In the past three decades, the Chinese living standard within the catchment grew each year. The value of the per capita intake of protein for each year was derived from Han et al. (2014) as 3.92, 4.67, 4.75 and 4.58 kg N per person in 1981, 1990, 2000, and 2009, respectively. We linearly interpolated the annual rate between available values for those years not reported.

Animals are usually fed according to relatively consistent dietary prescriptions designed for maintaining or gaining weight, and the N consumption per individual was then multiplied by the number of each animal type (Fig. 2c). The values for N consumption per individual animal were obtained from Han et al. (2011) and The Ministry of Environmental Protection of the People's Republic of China (MEP, 2009) (Table 2). The average animal population for a year was quantified using data on sales and inventory of livestock (Hong et al., 2013):

$$AL = inventory \times \frac{1}{Cycles} + \frac{Sales}{Cycles} \times \frac{Cycles - 1}{Cycles} \tag{2}$$

where *AL* is the annual average number of livestock, *inventory* is the end-of-year inventory number (Fig. 2c), *Sales* is the number of livestock slaughtered, which was derived from the annual yearbooks, and *Cycles* is the life cycle duration (the number of days from birth to market) per year, which is estimated as: 365/life cycle. The life cycle for each animal type was adopted from Wang et al. (2006). We assumed all animals were completely formula fed, i.e., 50% from corn and 50% from pasture (Han et al., 2014).

Domestic animal N production was the difference between animal N consumption and excretion. The N excretion rates were obtained from reports for eastern China by The Ministry of Environmental Protection of the People's Republic of China (MEP, 2009) (Table 2). It was assumed that spoilage and inedible components resulted in a 10% loss of animal products available for consumption (Han et al., 2011).

Crop N production was estimated by multiplying the yield of a specific crop by its N content (Table 2, Wang, 2003). Considering that the N content in different vegetables is only slightly different, we used the N content of cabbage to represent all of the vegetable crops grown in the catchment (Wang, 2003). We assume that pests, spoilage, and processing cause a 10% loss of consumption for all crops (Han et al., 2014).

#### 2.3.6. Uncertainty analysis

To gain insight into the uncertainty in the NANI estimation, an uncertainty analysis was performed using Monte Carlo simulation, which utilized a random sampling from predetermined probability distribution functions for parameters as input (Jiang et al., 2013).

**Table 1**
Biological N fixation rates and seed N input rates for different agricultural lands.

| N fixation rate (kg N ha$^{-1}$ yr$^{-1}$) | | Seed N input rate (kg N ha$^{-1}$ yr$^{-1}$) | | | |
|---|---|---|---|---|---|
| Land types | N fixation | Crop type | Seed N input | Crop type | Seed N input |
| Green manure | 150 | Rice | 0.69 | Peanuts | 0.35 |
| Leguminous plants | 64 | Wheat | 2.27 | Vegetables | 0.03 |
| Paddy field | 45 | Corn | 0.26 | | |
| Dryland | 15 | Potato | 1.07 | | |
| Garden plot | 15 | Soybeans | 1.08 | | |

**Table 2**
Domestic animal N consumption and excretion rates and N content of agricultural crops.

| Animal N consumption and excretion (kg N individual$^{-1}$ yr$^{-1}$) | | | | N content of crop production (g kg$^{-1}$) | | | |
|---|---|---|---|---|---|---|---|
| Animal type | N consumption | N excretion | Production N | Crop type | N content | Crop type | N content |
| Pigs and hogs | 16.7 | 11.5 | 5.17 | Rice | 11.8 | Vegetables | 2.6 |
| Cattle | 54.8 | 48.8 | 6.03 | Corn | 14.1 | Fruits | 0.59 |
| Sheep | 6.85 | 5.75 | 1.10 | Wheat | 17.9 | | |
| Chickens | 0.57 | 0.37 | 0.20 | Potato | 3.2 | | |
| Duck | 0.63 | 0.41 | 0.22 | Peanuts | 19.4 | | |
| Aquatic products (g kg$^{-1}$) | 34.4 | 4.96 | 29.4 | Soybeans | 56.2 | | |

Due to the limited number of parameter values available in the literature for NANI estimation, it is difficult to directly determine the probability distribution type and statistical characteristics (i.e., mean and standard deviation) for each parameter (Supplementary material A: Table A.1) as well as the dependences (correlation) among them by statistical analysis. In performing the Monte Carlo simulation for this study, we assumed that all the parameters used in the NANI estimation followed a normal distribution with the coefficient of variation of 30% for each of the parameters, which has been widely applied in watershed N budgeting studies conducted in nearby regions (Yan et al., 2011; Ti et al., 2012). Monte Carlo sampling randomly generated 10,000 sets of model parameters according to their normal distribution functions, resulting in 10,000 samples of NANI for each year. All input parameters (Supplementary material A: Table A.1) were set to be independent of each other during the Monte Carlo sampling, since the majority of them have no cause-and-effect relationships between each other in theory at least. The NANI estimation procedure was formulated in Microsoft Excel 2007 embedded with Crystal Ball software (Professional Edition 2000, Oracle Ltd. US., 2000) to run Monte Carlo simulations.

## 3. Results and discussion

### 3.1. Historical trend in riverine DIN exports

For daily $NH_4$–N, $NO_3$–N, and $NO_2$–N fluxes, a LOADEST model Eq. (1) with 7 unknown parameters ($\beta_0$, $\beta_1$, $\beta_2$, $\beta_3$, $\beta_4$, $\beta_5$, and $\beta_6$) provided the best Akaike information criterion and Schwarz criterion among the various formats of LOADEST regressions (Table 3) (Posada and Buckley, 2004), suggesting that Eq. (1) was the best model for characterizing daily nitrogen fluxes. All calibrated parameters for the $NH_4$–N, $NO_3$–N, and $NO_2$–N flux models were statistically significant ($p < 0.05$) (Table 3). Both $R^2$ and Nash–Sutcliffe efficiencies for the $NH_4$–N, $NO_3$–N, and $NO_2$–N flux models were greater than 0.80 (Fig. 3 and Table 3), indicating that a satisfactory fraction of the variance was explained by the regressions. The Durbin-Watson statistic for each model's residuals ranged from 1.313 to 1.851, which falls within the range of 1–3, indicating that the residuals were independent of input variables (Alkorta et al., 2000). These assessment indexes validate the use of the LOADEST model for estimating annual DIN concentrations and yields.

Using the calibrated LOADEST model, estimated annual average DIN concentration steadily increased from 0.42 mg N L$^{-1}$ in the 1980s to 0.55 mg N L$^{-1}$ in the 1990s, and then rapidly increased to 0.82 mg N L$^{-1}$ in the 2000s (Fig. 4a). The average DIN concentration in the 1980s, 1990s and 2000s was 3.5-fold, 4.6-fold, and 6.8-fold greater than natural background DIN levels observed in various pristine rivers worldwide (Meybeck, 1982), respectively. Similar to DIN concentration, annual riverine DIN yields increased 1.6-fold over the 31-yr study period (Fig. 4a), from an average 3.8 kg N ha$^{-1}$ yr$^{-1}$ in the 1980s, to 5.3 kg N ha$^{-1}$ yr$^{-1}$ in the 1990s, and to 6.7 kg N ha$^{-1}$ yr$^{-1}$ in the 2000s. Nitrate represented more than 80% of DIN over the 1980–1999 period, but its contribution decreased from 88% to 29% in the 2000s (Fig. 4b). In contrast to $NO_3^-$, $NH_4^+$ represented < 15% of DIN over the 1980–1999 period, while its contribution increased from 10% to 64% in the 2000s (>50% after 2008). Since $NH_4^+$ is held in the soil by cation exchange reactions, it has limited mobility from agricultural lands as compared to $NO_3^-$ (Swaney et al., 2012). Thus, the increasing $NH_4^+$ concentrations are likely originating from increasing human sewage and animal waste sources (Howarth, 2008; Swaney et al., 2012) due to increasing population density and poultry production (Fig. 2b). As expected, $NO_2^-$ always accounted for a very limited proportion of DIN (~3%).

### 3.2. Historical trends in NANI budgets

In the upper Jiaojiang catchment, NANI increased from 38.0 kg N ha$^{-1}$ yr$^{-1}$ in 1980 to 77.6 kg N ha$^{-1}$ yr$^{-1}$ in 2000 before declining to 67.3 kg N ha$^{-1}$ yr$^{-1}$ in 2010, resulting in a 77% net increase over the 31-yr study period (Fig. 5). On average, NANI increased by 102% during the 1980–1999 time period, but decreased by 13% during the 2000–2010 time period. The decrease in NANI mainly resulted from decreased chemical N fertilizer application since 2000 (Fig. 5). Due to the high woodland percentage (~67%), the NANI for the upper Jiaojiang catchment was lower than the average NANI reported for Zhejiang Province, China (70.4 kg N ha$^{-1}$ yr$^{-1}$ in 1981 to 110 kg N ha$^{-1}$ yr$^{-1}$ in 2009; Han et al., 2014). Annual NANI was positively correlated with annual population density ($R^2 = 0.82$, $p < 0.01$), agricultural land area percentage ($R^2 = 0.46$, $p < 0.01$), and developed land area percentage ($R^2 = 0.85$, $p < 0.01$), while it was negatively correlated with

**Table 3**
The calibrated parameters of LOADEST models for daily $NH_4$–N, $NO_3$–N, and $NO_2$–N fluxes and model performance assessment.

| Nitrogen form | Parameters | Values | Sig. | Performance assessment |
|---|---|---|---|---|
| $NH_4$–N | $\beta_0$ | 4.216 | <0.001 | Akaike info criterion = 2.70 |
| | $\beta_1$ | 0.993 | <0.001 | Schwarz criterion = 2.79 |
| | $\beta_2$ | 0.021 | 0.028 | $R^2$ = 0.81 ($n$ = 300) |
| | $\beta_3$ | 0.149 | <0.001 | Nash–Sutcliffe efficiency = 0.82 |
| | $\beta_4$ | 0.012 | <0.001 | Durbin-Watson stat = 1.31 |
| | $\beta_5$ | −0.035 | 0.018 | |
| | $\beta_6$ | 0.034 | 0.012 | |
| $NO_3$–N | $\beta_0$ | 6.352 | <0.001 | Akaike info criterion = 1.71 |
| | $\beta_1$ | 1.039 | <0.001 | Schwarz criterion = 1.82 |
| | $\beta_2$ | 0.012 | <0.001 | $R^2$ = 0.83 ($n$ = 212) |
| | $\beta_3$ | 0.007 | 0.026 | Nash–Sutcliffe efficiency = 0.84 |
| | $\beta_4$ | −0.002 | <0.001 | Durbin-Watson stat = 1.55 |
| | $\beta_5$ | −0.190 | 0.042 | |
| | $\beta_6$ | 0.048 | <0.001 | |
| $NO_2$–N | $\beta_0$ | 1.886 | <0.001 | Akaike info criterion = 1.28 |
| | $\beta_1$ | 1.036 | <0.001 | Schwarz criterion = 1.41 |
| | $\beta_2$ | 0.023 | 0.043 | $R^2$ = 0.80 ($n$ = 192) |
| | $\beta_3$ | 0.086 | <0.001 | Nash–Sutcliffe efficiency = 0.81 |
| | $\beta_4$ | 0.010 | <0.001 | Durbin-Watson stat = 1.85 |
| | $\beta_5$ | −0.029 | 0.038 | |
| | $\beta_6$ | 0.248 | <0.001 | |

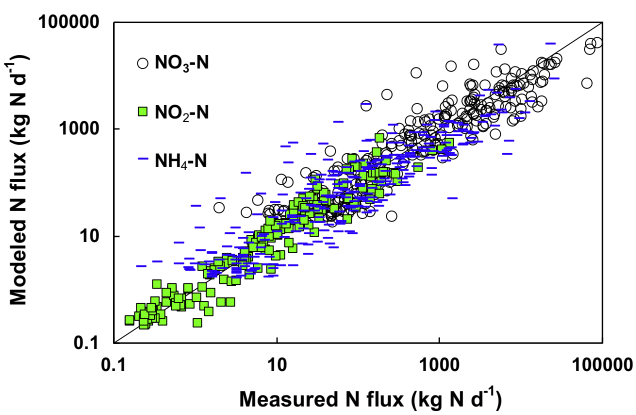


**Fig. 3.** Daily $NH_4$–N, $NO_3$–N, and $NO_2$–N fluxes showing observed vs modeled values using the LOADEST model in the upper Jiaojiang River.

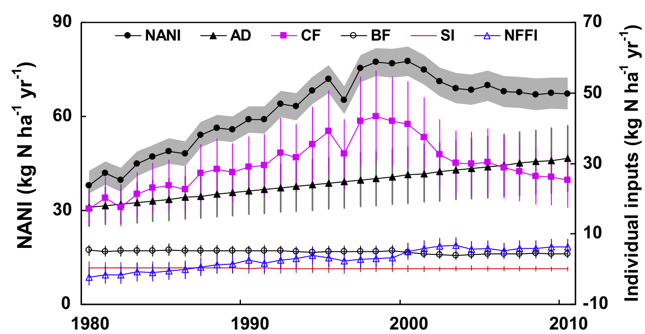


**Fig. 5.** Historical trend in net anthropogenic N input (NANI) from atmospheric deposition (AD), chemical fertilizer (CF), biological N fixation (BF), seed input (SI), and net food and feed input (NFFI) in the upper Jiaojiang River catchment over the 1980–2010 period. Shadow area and vertical line denotes 95% confidence interval of NANI and individual input components, respectively.

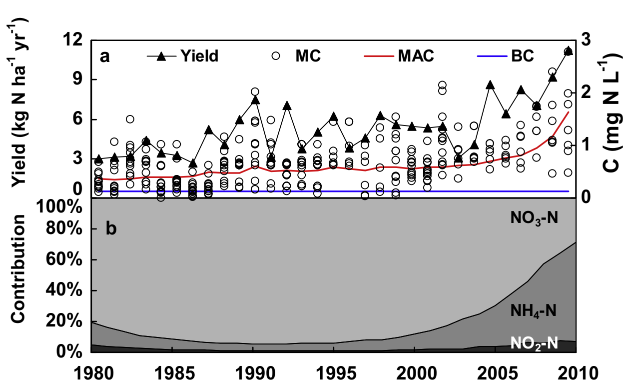


**Fig. 4.** Historical trends in DIN yield, measured concentration (MC), and modeled annual average concentration (MAC), as well as natural background DIN concentration observed in various pristine rivers worldwide (Meybeck, 1982) (a), and contributions of $NH_4^+$, $NO_3^-$, and $NO_2^-$ to DIN (b) in the upper Jiaojiang River over the 1980–2010 period.

woodland percentage ($R^2$ = 0.53, $p$ < 0.01), consistent with other studies (Han et al., 2009; Han et al., 2011).

Over the 1980–2010 period, chemical N fertilizer (48%) and atmospheric N deposition (40%) were the major sources of NANI (Fig. 5). However, chemical N fertilizer application and agricultural biological N fixation decreased by 40% and 8% since 2000, respectively, due to decreased cropland cultivation (44%) between 2000 and 2010 (Fig. 2b). Seed N input, which only accounted for 0.4% (ranging from 0.9% in 1980 to 0.1% in 2010) of NANI and 1.5% (ranging from 2.1% in 1980 to 0.9% in 2010) of crop N production, rapidly decreased by 70% from 1980 to 2010. On the other hand, net food and feed N import/export increased remarkably from -1.9 kg N ha$^{-1}$ yr$^{-1}$ in 1980 to 6.5 kg N ha$^{-1}$ yr$^{-1}$ in 2010, implying that the upper Jiaojiang catchment changed from an autotrophic (a producer of biomass) to heterotrophic (a consumer of biomass) net N balance (Howarth et al., 2012; Swaney et al., 2012). This increasing trend indicated that N flow from sewage and animal manures that originated as imported food and feed was increased to support increasing human population and livestock production (Fig. 2c). The increasing human sewage and animal wastes are consistent with the observed upward trend in $NH_4^+$ proportion to DIN over the study period (Fig. 4b). Due to their higher N input magnitudes, atmospheric deposition and chemical fertilizer application rate presented larger 95% confidence intervals than other inputs (Fig. 5). This suggests that they are responsible for most of the uncertainty in estimating NANI and improving the accuracy of the parameters used to estimate these two components (such as

N content in various fertilizer types and atmospheric N deposition rate, Table A.1) would be most effective for reducing NANI uncertainty.

### 3.3. Riverine DIN export in relation to individual factors

In the upper Jiaojiang catchment, annual riverine DIN yield was positively correlated with NANI and their relationship could be best described by an exponential function over the 1980–2010 period (Table 4), consistent with other studies (McIsaac et al., 2001, 2002; Han et al., 2009). However, riverine DIN yield (Fig. 4a) and NANI (Fig. 5) presented a contrasting trend over the 2000–2010 period, implying changes in N storage/removal efficiency and/or increased fractional delivery of NANI due to changing land-use, since no significant increasing trends in hydroclimate were observed in the 2000s (Fig. 2a). Riverine DIN yield was also significantly correlated with net food and feed N input and atmospheric N deposition (Table 4), while it was not correlated with other individual inputs. The positive correlation for net food and feed N input is driven by increased sewage and animal wastes from imported food/feeds required to support increasing human population and livestock production over the study period (Fig. 2c), consistent with the increasing proportion and concentration of $NH_4^+$ observed in the river (Fig. 4b). Similar results have been reported for other major watersheds in China, such as the Yangzi River, Yellow River and Zhujiang River watersheds (MOA, 2004; Ti et al., 2012). An exponential increase in riverine DIN yield with increasing atmospheric N deposition is associated with its increasing contribution to NANI due to the high woodland area percentage (~67%) in this catchment, implying an increasing degree of N saturation for woodlands over time due to increasing atmospheric N deposition (Howarth et al., 2012).

Compared to NANI, river discharge (32% NANI vs 44% discharge) and precipitation (32% NANI vs 53% precipitation) explained a larger portion of variability in annual riverine DIN yield (Table 4). Furthermore, riverine DIN yield exhibited higher correlations with developed land (32% NANI vs 53% developed land) and agricultural land (32% NANI vs 47% agricultural land) area percentages than with NANI (Table 4). Similar results were found in the Thames (UK) and Mississippi (USA) watersheds, where changes in riverine N concentration or flux over time was attributed to changes in delivery related to changes in flow regime and land-use rather than annual N inputs (McIsaac et al., 2001; Edwards and Withers, 2008; Howden et al., 2010). These results are typically due to higher storage of N in aquifers, soils and/or biomass in years with low runoff or less land disturbance, followed by flushing or release of stored N in years with higher runoff or more land disturbance (Howarth et al., 2006; Han et al., 2011; Howarth et al., 2012). Van Breemen et al. (2002) reported that ~27% of annual NANI was stored in soils and woody biomass in 16 catchments in the northeastern USA. Field studies conducted in surrounding regions in China showed that 2–6% of the applied chemical fertilizer and manure N per season was added to groundwater storage (Yan et al., 2011; Ti et al., 2012). All of these study results imply that a portion of the annual anthropogenic N inputs can be temporarily stored within the catchment, which has the potential to leach N to rivers in subsequent years.

The high dependence of annual riverine DIN yield on the developed land area is attributed to increased fractional export of NANI to rivers due to decreased N retention capacity and enhanced flushing effects during rainfall events, since developed lands have a greater impervious surface area resulting in greater runoff to surface waters (Groffman et al., 2004; Kaushal et al., 2008). Furthermore, the higher export of NANI and stored N to rivers in years with higher rainfall/runoff and more developed land area may reduce denitrification in hot spots, such as riparian wetlands and low-order streams, due to shorter water residence times in these systems (Elmore and Kaushal, 2008; Han et al., 2009; Chen et al., 2013). The significant correlation between annual riverine DIN yield and agricultural land area was due to the high dependence of chemical N fertilizer application on agricultural land area (Fig. 2b), since inorganic N fertilizers may be more readily transported to surface waters than organic N forms (McIsaac et al., 2002).

### 3.4. Riverine DIN exports in relation to combined factors

The analyses reported above indicate that year-to-year variation of riverine DIN yield was strongly related to NANI, land-use, and hydroclimate, suggesting that the integrated influence of these factors should be considered in developing models for riverine DIN export. As this study (Table 4) and previous studies have shown, the relationship between riverine N export and NANI is best described using an exponential function and the relationship between riverine N export and discharge is best described using a power function (McIsaac et al., 2001 and 2002; Han et al., 2009); thus we developed the following model for annual riverine DIN yield ($F$, kg N ha$^{-1}$ yr$^{-1}$):

$$F = a(xy)^b \exp(c\text{NANI}) \tag{3}$$

where $x$ is annual average discharge ($Q$, m$^3$ s$^{-1}$) or precipitation ($P$, mm yr$^{-1}$), $y$ is developed land area percentage ($D$), or agricultural land area percentage ($A$), and $\alpha$, $b$, and $c$ are unknown parameters. Expressing Eq. (3) in a linear form after logarithmic transformation yields:

$$Ln(F) = Ln(a) + bLn(xy) + c\text{NANI} \tag{4}$$

The three unknown parameters ($\alpha$, $b$, and $c$) were calibrated using six combinations of the various factors in logarithmic format as shown in Eq. (4). Compared to individual variables, the combined NANI and either precipitation or discharge explained annual riverine DIN export with reasonably high accuracy ($R^2$ = 0.67–0.69) (Table 5). These model results compare favorably with those for other watersheds (Howarth et al., 2006). As expected, the predictive capability was further improved by combining NANI, hydroclimate, and land use ($R^2$ = 0.79–0.89). Among them, the

**Table 4**
Best regressions between riverine DIN yields ($F$, kg N ha$^{-1}$ yr$^{-1}$) and individual independent variables in the upper Jiaojiang catchment in 1980–2010 ($n$ = 31).

| Independent variables | Formulas | $R^2$ | $p$ |
|---|---|---|---|
| NANI (kg N ha$^{-1}$ yr$^{-1}$) | $F = 1.5736\exp(0.0185x)$ | 0.32 | <0.01 |
| Atmospheric deposition (kg N ha$^{-1}$ yr$^{-1}$) | $F = 1.0832\exp(0.0624x)$ | 0.47 | <0.01 |
| Net food and feed input (kg N ha$^{-1}$ yr$^{-1}$) | $F = 3.8602\exp(0.0875x)$ | 0.42 | <0.01 |
| Discharge (m$^3$ s$^{-1}$) | $F = 0.0752x^{0.9826}$ | 0.44 | <0.01 |
| Precipitation (mm yr$^{-1}$) | $F = 0.6577\exp(0.0014x)$ | 0.53 | <0.01 |
| Developed land area percentage | $F = 343.75x - 4.1284$ | 0.53 | <0.01 |
| Agricultural land area percentage | $F = 156.53x - 14.25$ | 0.47 | <0.01 |
| Woodland area percentage | $F = 1.0469x^{-3.8589}$ | 0.14 | <0.05 |

**Table 5**
Regression models for riverine DIN exports as an exponential function of NANI and a power function of various combinations of discharge ($Q$, m$^3$ s$^{-1}$), precipitation ($P$, mm yr$^{-1}$), developed land ($D$) and agricultural land ($A$) area percentages as shown in Eq. (4) for the upper Jiaojiang catchment in 1980–2010 ($n$ = 31).

| Combinations | Parameters | Values | Std. | $P$ | 2.5% | 97.5% | $R^2$ |
|---|---|---|---|---|---|---|---|
| NANI and $Q$ | $a$ | 0.034 | 0.007 | <0.001 | 0.009 | 0.132 | 0.69 |
| | $b$ | 0.923 | 0.151 | <0.001 | 0.614 | 1.231 | |
| | $c$ | 0.017 | 0.003 | <0.001 | 0.010 | 0.024 | |
| **NANI, $Q$, and $D$** | **$a$** | **1.147** | **0.127** | **0.0289** | **0.885** | **1.487** | **0.89** |
| | **$b$** | **0.014** | **0.002** | **<0.001** | **0.010** | **0.018** | |
| | **$c$** | **0.932** | **0.074** | **<0.001** | **0.780** | **1.085** | |
| NANI, $Q$, and $A$ | $a$ | 0.197 | 0.0258 | <0.001 | 0.116 | 0.334 | 0.84 |
| | $b$ | 1.065 | 0.107 | <0.001 | 0.846 | 1.285 | |
| | $c$ | 0.015 | 0.002 | <0.001 | 0.010 | 0.019 | |
| NANI and $P$ | $a$ | $5.802 \times 10^{-6}$ | $0.219 \times 10^{-4}$ | <0.001 | $0.065 \times 10^{-6}$ | $0.517 \times 10^{-3}$ | 0.67 |
| | $b$ | 1.769 | 0.308 | <0.001 | 1.137 | 2.400 | |
| | $c$ | 0.014 | 0.004 | 0.001 | 0.007 | 0.021 | |
| NANI, $P$, and $D$ | $a$ | 0.033 | 0.005 | <0.001 | 0.012 | 0.091 | 0.79 |
| | $b$ | 1.191 | 0.144 | <0.001 | 0.896 | 1.486 | |
| | $c$ | 0.011 | 0.003 | 0.001 | 0.005 | 0.017 | |
| NANI, $P$, and $A$ | $a$ | $0.266 \times 10^{-3}$ | $0.098 \times 10^{-3}$ | <0.001 | $0.036 \times 10^{-3}$ | $1.977 \times 10^{-3}$ | 0.81 |
| | $b$ | 1.785 | 0.198 | <0.001 | 1.378 | 2.191 | |
| | $c$ | 0.010 | 0.003 | 0.001 | 0.004 | 0.016 | |

The bold values are used in this study.

combination of NANI, discharge, and developed land area percentage best described year-to-year variability of riverine DIN export (Table 5):

$$F = 1.147(QD)^{0.932}\exp(0.014NANI) \tag{5}$$

Eq. (5) accounted for 89% of the variation in annual DIN yields over the 1980–2010 period (as shown by the $R^2$ of 0.89 between modeled mean DIN yields and LOADEST estimated values in Fig. 6a). Relative error of prediction accuracy for individual years was less than 9% and the interquartile range for each year was relatively symmetrical, typically ranging from -25% to + 25%. Considering the complexities of N biogeochemistry and transport in terrestrial landscapes and streams, the performance of the model Eq. (5) is very reasonable (Han et al., 2009; Chen et al., 2013). When we further replaced the $(xy)^b$ term in Eq. (3) with a term of $x^by^c$, the performance of the resulting models was inferior (Supplementary material B: Table A.2), implying that the influence of land-use pattern on N delivery from landscapes to the river should be jointly expressed by hydroclimate (e.g., change of land-use would not influence the fractional export of NANI significantly during the dry period when river water is mainly supplied by groundwater). Furthermore, the performance of regression models with an exponential function between riverine DIN export and NAIN was better than those with a linear function ($R^2$ = 0.67–0.89 vs 0.53–0.72 and relative error = ± 9%– ± 21% vs ± 16%– ± 28%)

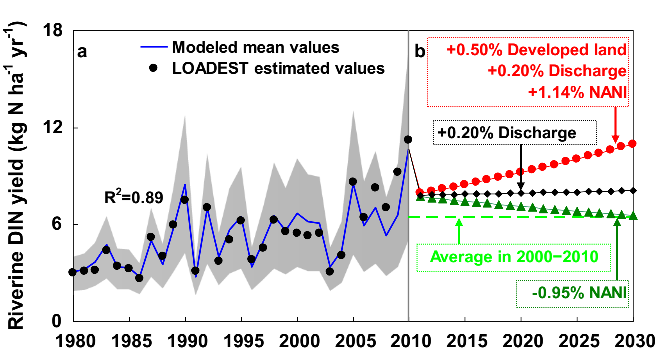


**Fig. 6.** The LOADEST estimated riverine DIN yield vs modeled values using Eq. (5) in 1980–2010 (a) and predicted future (2011–2030) DIN yield changes under three scenarios (b) in the upper Jiaojiang catchment. Shadow area denotes 95% confidence interval for modeled riverine DIN yield.

(Table 5 and Supplementary material B: Table A.2), implying an increasing degree of N saturation for the landscapes over time due to increasing NANI (McIsaac et al., 2001; Swaney et al., 2012). These comparisons suggested that Eq. (5) is the best model to describe the variation of riverine DIN yield in response to changes in NANI, land-use, and hydroclimate for this study catchment. Although this model lacks the ability to predict seasonal or daily river N export and differentiate among possible fates of N compared to more complex models, such as SWAT and SPARROW (Chen et al., 2013), it has the advantage of simplicity and can easily be applied to predict riverine DIN export from watershed anthropogenic N inputs, hydroclimate, and land use.

### 3.5. Riverine DIN sources apportionment

In previous studies using a linear or exponential relationship to model riverine N export from multi-year average NANI (i.e., eliminating temporal storage effect), riverine N sources were commonly apportioned to NANI and natural background sources (i.e., predicted exports when NANI = 0) (Howarth, 2008; Howarth et al., 2012; Han et al., 2009). The year-to-year model Eq. (5) developed here implies a storage effect on annual riverine DIN export. Using Eq. (5), annual riverine DIN export was apportioned to NANI in the present year ($F_{NANI}$), storage sources ($F_S$), and natural background sources ($F_B$). Predicted DIN export yield calculated by Eq. (5) when NANI was set equal to zero represents the amount of DIN derived from $F_S$ and $F_B$. Thus, DIN export derived from NANI in the present year ($F_{NANI}$) can be estimated as:

$$F_{\mathrm{NANI}} = 1.147(QD)^{0.932}\exp(0.014\mathrm{NANI}) - 1.147(QD)^{0.932} \tag{6}$$

To further distinguish $F_S$ and $F_B$, we assumed that annual natural background export is a function of discharge and the average DIN concentration observed in pristine rivers ($C_b$ = 0.12 mg N L$^{-1}$, Meybeck, 1982). This approach is supported by studies showing that the observed riverine N export strongly depends on annual discharge in a number of minimally disturbed watersheds (Lewis et al., 1999; Howarth et al., 2006; Han et al., 2009). Then $F_S$ can be estimated as:

$$F_S = 1.147(QD)^{0.932} - \frac{86.4NQC_b}{A} \tag{7}$$

where $N$ is the number of days in a year (i.e., 365 or 366), $A$ is the catchment area (ha), and 86.4 is a conversion factor. To address uncertainty, a 30% coefficient of variation was assumed for $C_b$ (i.e., 95% confidence interval: 0.084–0.156 mg N $L^{-1}$) and the 95% confidence interval for parameters $a$ and $b$ in Eq. (5) (Table 5) were applied to a total of 10,000 Monte Carlo simulations for Eq. (7) to get annual $F_S$ values.

In the upper Jiaojiang catchment, annual NANI ($F_{NANI}$) contributed 57% (range: 41–66%) of riverine DIN exports for a given year over the 1980–2010 period on average, while storage sources ($F_S$) and natural background sources ($F_B$) contributed 22% (range: 15–31%) and 21% (range: 14–32%), respectively (Fig. 7). Estimated mean DIN export from natural background sources of 1.08 kg N $ha^{-1}$ $yr^{-1}$ (range: 0.58–1.81 kg N $ha^{-1}$ $yr^{-1}$) is comparable with results for total N from previous studies (i.e., 0.67–2.78 kg N $ha^{-1}$ $yr^{-1}$), which take the intercept value of the linear regression between multi-year average NANI and river total N export as the natural background level (Howarth, 2008; Howarth et al., 2012; Han et al., 2009).

As expected, the $F_S$ comprised a considerable proportion (~22%) of annual riverine DIN export in this study catchment, which is well supported by results from both field and watershed scales studies. These previous studies assigned 25–40% of the annual N flux to mineralization of soil organic N (Booth et al., 2005; Kopáček et al., 2013) and 30–40% to $NO_3^-$ exported from groundwater (Iqbal, 2002; Lindsey et al., 2003). Given the time scale for soil N mineralization and hydrologic processes, the influence of the storage effect could last from several years to several decades (Iqbal, 2002; Stålnacke et al., 2003; Lindsey et al., 2003; Howden et al., 2010). These results imply that a portion of the DIN flux may be derived from storage sources originating from NANI to the catchment before the 1980–2010 study period. Due to the unknown time duration of the storage effect, there is a considerable uncertainty when determining fractional NANI exported by rivers based on the average NANI value for an objectively selected interval of years. Thus, more research is required to evaluate the storage effect on watershed N budgets and riverine N flux dynamics.

### *3.6. Forecasting future riverine DIN exports*

To predict future riverine DIN exports for the 2011–2030 period using the developed model Eq. (5), we took average NANI and discharge in 2000–2010 and the developed land area in 2010 as the baseline conditions. We forecasted future trends of NANI, discharge, and developed land area based on three scenarios. The "climate change" scenario projects an increase of discharge by 4% in 2030 (i.e., ~0.2% increase per year, Han et al., 2009) with no change in NANI or land-use. Under the "tackling" scenario, NANI in 2030 (~57.1 kg N $ha^{-1}$ $yr^{-1}$) would be 18.2% less than average NANI in 2000–2010 with no change in discharge or land use, based on "The Response Program for Climate Change of Zhejiang Province in China" (PGZP, 2010). The "developing" scenario projected a 22% increase of NANI and a 10% increase of developed land area by 2030 (consistent with trends measured during the 1980–2010 study period) coupled with a 2% increase of discharge relative to average values in 2000–2010.

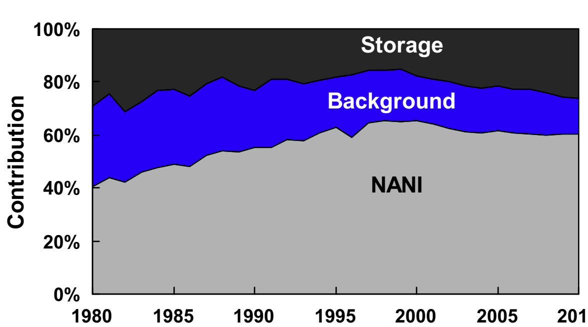


**Fig. 7.** The contributions of present year NANI, catchment N storage derived from NANI in previous years, and natural background sources to observed annual riverine DIN export in 1980–2010 in the upper Jiaojiang catchment.

The climate change scenario predicted a 19.6% increase of future riverine DIN yield in 2030 relative to the average value (i.e., 6.4 kg N $ha^{-1}$ $yr^{-1}$) for the 2000–2010 baseline period (Fig. 6b), resulting from greater fractional delivery of both NANI and stored N as water discharge increased. This result is consistent with predictions for the Susquehanna River basin (USA) where a 2% increase in discharge resulted in a 17% in riverine N by 2030 (Howarth et al., 2006). Under the tackling scenario, riverine DIN yield in 2030 decreased by 15.2% due to an 18.2% reduction of NANI from 2011 to 2030. Under the developing scenario, DIN yield increased by 70.8% in 2030 compared to the average value for 2000–2010. Although these predictions are subject to uncertainties in future N inputs and climate change as well as storage sources, the predicted results under the tackling and developing scenarios roughly represent the upper and lower bounds for future riverine DIN exports in response to anthropogenic activities and climate change. These riverine N yield bounds provide a baseline for assessing and adopting relevant watershed N management strategies. Climate change is predicted to have an impact on increasing DIN export from the upper Jiaojiang River catchment, aggravating N pollution in the coastal waters of Jiaojiang Bay. This suggests that the influence of climate change on riverine DIN exports should be considered as part of management efforts to control coastal N pollution.

## 4. Conclusion

This study presents the first historically explicit analysis of N inputs and riverine export for a typical watershed in eastern China that has undergone tremendous economic development in the last three decades. In the upper Jiaojiang River catchment, riverine DIN yield increased by about 1.6-fold over the 1980–2010 period and the proportion of $NH_4^+$ to DIN increased from 4–15% in 1980–1999 to 15–64% in 2000–2010. These changes resulted from increasing NANI (especially net food/feed input) and increasing fractional delivery of NANI enhanced by increasing developed land area. Due to the catchment N storage effect, NANI explained less variations in annual riverine DIN export than hydroclimate (i.e., discharge or precipitation) and disturbed land area percentages (i.e., developed and agricultural lands). Using an empirical model for the riverine N yield ($R^2$ = 0.89) that incorporates NANI, water discharge, and developed land area percentage, annual NANI, catchment N storage, and natural background sources were determined to account for 57%, 22%, and 21%, respectively, of the observed annual riverine DIN export. Riverine DIN export is predicted to increase by 19.6% by 2030 compared to the 2000–2010 baseline condition in response to the 4% increase in annual discharge predicted for the climate change scenario, even with no changes in NANI and land use. These results highlight that anthropogenic activities have increased both the N amount available for export and the fractional export of N inputs by river, while climate change can further enhance N export. An integrated N management strategy considering the influence of anthropogenic N inputs, land use, and climate change is required to assess and optimize N management strategies for protecting coastal waters.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhydrol.2014.05.024.

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