Net anthropogenic nitrogen inputs (NANI) into the Yangtze River basin and the relationship with riverine nitrogen export

Article *in* Journal of Geophysical Research: Biogeosciences · February 2016

DOI: 10.1002/2015JG003186

AGU PUBLICATIONS

JGR

Journal of Geophysical Research: Biogeosciences

RESEARCH ARTICLE
10.1002/2015JG003186

Fei Chen and Lijun Hou equally contributed to this work.

Key Points:
- NANI has increased by more than twofold from 1980 to 2012
- Chemical fertilizer application was the largest component of NANI in the basin
- The riverine DIN export was strongly correlated with NANI

Supporting Information:
- Supporting Information S1

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Citation:
Chen, F., et al. (2016), Net anthropogenic nitrogen inputs (NANI) into the Yangtze River basin and the relationship with riverine nitrogen export, *J. Geophys. Res. Biogeosci.*, *121*, doi:10.1002/2015JG003186.

Received 19 AUG 2015
Accepted 13 JAN 2016
Accepted article online 15 JAN 2016

Net anthropogenic nitrogen inputs (NANI) into the Yangtze River basin and the relationship with riverine nitrogen export

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Abstract This study investigated net anthropogenic nitrogen inputs (NANI, including atmospheric nitrogen deposition, nitrogenous fertilizer use, net nitrogen import in food and feed, and agricultural nitrogen fixation) and the associated relationship with riverine dissolved inorganic nitrogen (DIN) export in the Yangtze River basin during the 1980–2012 period. The total NANI in the Yangtze River basin has increased by more than twofold over the past three decades (3537.0 ± 615.3 to 8176.6 ± 1442.1 kg N km^{-2} yr^{-1}). The application of chemical fertilizer was the largest component of NANI in the basin (51.1%), followed by net nitrogen import in food and feed (26.0%), atmospheric nitrogen deposition (13.2%), and agricultural nitrogen fixation (9.7%). A regression analysis showed that the riverine DIN export was strongly correlated with NANI and the annual water discharge ($R^2 = 0.90$, $p < 0.01$). NANI in the Yangtze River basin was estimated to contribute 37–66% to the riverine DIN export. We also forecasted future variations in NANI and riverine DIN export for the years 2013 to 2030, based on possible future changes in human activities and the climate. This work provides a quantitative understanding of NANI in the Yangtze River basin and its effects on riverine DIN export and helps to develop integrated watershed nitrogen management strategies.

1. Introduction

In the past few decades, large quantities of anthropogenic nitrogen have been introduced into the biosphere through human activities, such as industrial fertilizer application, fossil fuel combustion, and crop cultivation [*Galloway et al.*, 1995; *Van Breemen et al.*, 2002]. On a global scale, the annual production of anthropogenic nitrogen has been estimated to be as much as 150 Tg N [*Arvin and Mosier*, 2000; *Galloway et al.*, 2003], which is almost equivalent to twice the natural input of fixed nitrogen in terrestrial ecosystems [*Galloway et al.*, 2004, 2008]. The increase in anthropogenic nitrogen has contributed greatly to food production. However, a substantial amount of anthropogenic nitrogen is transported to estuarine and coastal waters via river flow [*Seitzinger et al.*, 2010], consequently leading to numerous environmental and ecological issues, such as coastal eutrophication, hypoxia, harmful algae blooms, and a reduction in biodiversity [*Burgin and Hamilton*, 2007; *Diaz and Rosenberg*, 2008; *Canfield et al.*, 2010; *Deegan et al.*, 2012]. Therefore, it is important to understand and characterize the sources of anthropogenic nitrogen and their effects on riverine nitrogen export in order to develop watershed nitrogen pollution control strategies [*Gruber and Galloway*, 2008; *Swaney et al.*, 2012; *Hong et al.*, 2013; *Chen et al.*, 2014; *Han et al.*, 2014; *Sha et al.*, 2014].

Net anthropogenic nitrogen input (NANI) is a nitrogen budgeting approach that generally includes nitrogen supplies from atmospheric deposition, chemical fertilizer application, net nitrogen import in food and feed, and agricultural nitrogen fixation [*Howarth et al.*, 1996]. The NANI approach is recognized as an effective tool to estimate human-controlled nitrogen inputs to a watershed [*McIsaac et al.*, 2002; *Swaney et al.*, 2012; *Hong et al.*, 2013; *Han et al.*, 2014]. Since it was introduced by *Howarth et al.* [1996], NANI has been widely applied to identify the major sources of anthropogenic nitrogen in many regions across the U.S. [*Goolsby et al.*, 1999; *McIsaac et al.*, 2001, 2002; *Alexander et al.*, 2002; *Boyer et al.*, 2002; *Howarth et al.*, 2006, 2012; *Schaefer and Alber*, 2007; *Han and Allan*, 2008; *Han et al.*, 2009; *Schaefer et al.*, 2009; *Hong et al.*, 2011a, 2013], Europe [*Hägg*, 2010; *Billen et al.*, 2011; *Leip et al.*, 2011; *Hong et al.*, 2011b; *Kopáček et al.*, 2013] and Asia [*Hayakawa et al.*, 2009; *Chen et al.*, 2014; *Gao et al.*, 2014; *Huang et al.*, 2014; *Swaney et al.*, 2015]. Furthermore, NANI has been found to be a good predictor of riverine nitrogen fluxes from watersheds to estuarine and coastal waters [*Swaney et al.*, 2012; *Hong et al.*, 2013]. However, the relationship between NANI and riverine nitrogen export may also be affected by other factors in watersheds, such as the climate [*McIsaac et al.*, 2001; *Han et al.*, 2009; *Howarth et al.*, 2012; *Chen et al.*, 2014] and land use/land management practices [*Groffman et al.*, 2004; *Kaushal et al.*, 2008; *Sobota et al.*, 2009; *Huang et al.*, 2014].

The nitrogen exported from watersheds via rivers has been commonly apportioned to NANI and natural background nitrogen sources [*Howarth*, 2008; *Han et al.*, 2009; *Howarth et al.*, 2012; *Swaney et al.*, 2012]. However, numerous studies show that although most anthropogenic nitrogen imported into watersheds is exported by rivers or lost through denitrification, a considerable portion of the anthropogenic nitrogen may be retained in the soil, groundwater, or biomass [*Van Breemen et al.*, 2002; *Howarth et al.*, 2006; *Swaney et al.*, 2012]. This implies that the fraction of nitrogen retained in watersheds is a potential source for the future release of nitrogen into rivers [*Stålnacke et al.*, 2003; *Chen et al.*, 2014]. So far, several studies have reported that approximately 22–40% of the annual riverine nitrogen export may derive from the storage of NANI from previous years [*Kopáček et al.*, 2013; *Chen et al.*, 2014; *Huang et al.*, 2014]. Nevertheless, the respective contributions of NANI, nitrogen storage, and background nitrogen sources to riverine nitrogen export remain unclear for a specific watershed in a given year or period.

The Yangtze River is the largest river in the Euro-Asian continent and is ranked third in length, fourth in sediment discharge, and fifth in freshwater discharge in the world. The Yangtze River basin has played an important role in the economy of China and generates as much as half of China's gross domestic product (GDP) [*Lin et al.*, 2005]. However, human activities have caused an increasing load of anthropogenic nitrogen from fish farming and agricultural activities, as well as both industrial and domestic wastewater, to be discharged into the Yangtze estuarine and adjacent coastal areas in recent decades [*Zheng et al.*, 2013], which is considered the primary factor leading to severe eutrophication [*Zheng et al.*, 2014; *Deng et al.*, 2015]. Since the 1980s, harmful algal blooms have been occurring frequently in estuarine and coastal areas, mainly because of an overenrichment of dissolved inorganic nitrogen (DIN) [*Hou et al.*, 2006, 2013; *Wang et al.*, 2015]. In recent years, numerous studies have examined the riverine DIN fluxes from the Yangtze River to the estuary [*Yan et al.*, 2003; *Li et al.*, 2007; *Dai et al.*, 2011; *Gao et al.*, 2012; *Xu et al.*, 2013]. However, to our knowledge, few studies have identified the net human-induced nitrogen inputs to the Yangtze River basin and their relationships with riverine DIN export [*Yan et al.*, 2003; *Xu et al.*, 2013]. Using the NANI approach, the present work aims to analyze the temporal and spatial changes of NANI in the Yangtze River basin from 1980 to 2012, to discuss the potential links of NANI with riverine DIN fluxes and the occurrence of red tides in the Yangtze estuarine and coastal ecosystem, and to identify the respective contributions of NANI, watershed nitrogen storage, and natural background nitrogen sources to riverine DIN export. We also predict future trends in NANI and riverine nitrogen export for the years 2013 to 2030, based on possible future changes in human activities and the climate. This study provides a quantitative understanding of NANI in the Yangtze River basin and associated links with riverine nitrogen transport, which may help guide conservation, policy, and adaptive management efforts for protecting and/or restoring water quality.

2. Materials and Methods

2.1. Study Area

The Yangtze River lies between 90°–122°E and 24°–35°N. It flows for 6300 km from the glaciers on the Qinghai-Tibet Plateau in Qinghai eastward across southwest, central, and eastern China before emptying into the East China Sea at Shanghai (Figure 1). The Yangtze River has a total drainage area of approximately 1.8×10^6 km^2, which is approximately one fifth of China's land area [*Xing and Zhu*, 2002; *Liu et al.*, 2003]. According to the drainage basin characteristics of the Yangtze River, the entire basin is divided into 11 subcatchments, including Jinshajiang (JSJ), Mintuojiang (MTJ), Wujiang (WJ), the Upper mainstream region (UM), Jialingjiang (JLJ), Dongtinghu (DTH), the Middle mainstream region (MM), Hanjiang (HJ), Poyanghu (PYH), the Lower mainstream region (LM), and Taihu (TH). The properties of these subcatchments are summarized in Table 1, which include the drainage area, land use, annual average precipitation, GDP, and the total population amount and density. The areas of these subcatchments range from approximately 36,900 km^2 (TH) to 483,000 km^2 (JSJ). Over the 1980–2012 period, combined land use across the Yangtze River basin was about 30% agricultural, 40% forest, 24% grass, 3% wetland, and 1% urban. In general, relatively high urbanization has occurred in the eastern subcatchments.

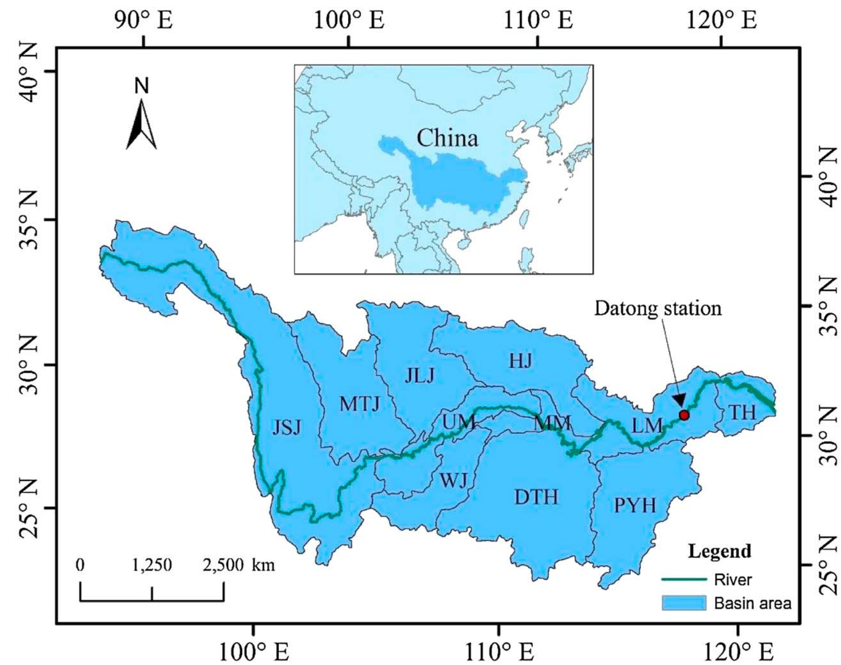

Figure 1. Geographic location of the Yangtze River basin and subcatchments. JSJ: Jinshajiang; MTJ: Mintuojiang; WJ: Wujiang; UM: Upper mainstream; JLJ: Jialingjiang; DTH: Dongtinghu; MM: Middle mainstream; HJ: Hanjiang; PYH: Poyanghu; LM: Lower mainstream; TH: Taihu.

2.2. NANI Estimation and Uncertainty Analysis

In this study, the NANI calculation was based on the conceptual model developed by *Howarth et al*. [1996]. The model is composed mainly of four components: fertilizer nitrogen application, atmospheric nitrogen deposition, net nitrogen import in food and feed, and agricultural nitrogen fixation. The data for the NANI calculation mainly included land use area, rural and urban and livestock populations, crop products, animal production, atmospheric nitrogen deposition, and fertilizer use. In this study, an area-weighting method was applied to extrapolate these data from administrative regions to subcatchment areas. This extrapolation was performed with an ArcGIS tool via overlaying a subcatchment map with various data maps to calculate the overlying proportions [*Hong et al*., 2011b]. Here we calculated the NANI of each catchment for the years 1980, 1985, 1990, 1995, 2000, 2005, 2010, and 2012. The unit for all components of NANI is expressed as kg N per km^2 of area per year.

Table 1. Characteristics (Averaged From 1980 to 2012) for Subcatchments of the Yangtze River Basin[a]

Subcatchment	Area (km^2)	Precipitation (mm)	Total Population (10^4 Individual)	Population Density (Individual km^{-2})	Population Percent Increase (%)	GDP (10^8 \$)	Land Use (%)					
							Agriculture	Forest	Grass	Urban	Wetland	Other
JSJ	483,000	706	4,184	87	32	588	21	30	40.6	0.46	2.3	5.9
MTJ	170,000	1,083	7,159	421	27	1,024	26	33	35.6	0.54	1.1	3.46
WJ	88,000	1,164	3,556	404	49	391	34	50	14.8	0.6	0.8	0.02
UM	99,550	1,169	4,766	479	33	724	33	37	25.8	0.81	1.5	1.83
JLJ	159,800	965	5,692	356	29	808	27	34	34.7	0.57	0.9	2.78
DTH	257,200	1,414	5,878	229	37	969	32	58	5	1.16	3.6	0.02
MM	96,000	1,243	5,415	564	23	1,056	41	46	4.2	2.42	5.9	0.04
HJ	160,000	900	5,348	334	36	950	37	41	15.9	1.97	3.9	0.07
PYH	162,200	1,598	4,267	263	39	766	31	58	4.6	1.47	4.9	0.02
LM	91,000	1,158	5,871	645	38	1,199	50	32	6.4	4.43	7.5	0.02
TH	36,900	1,105	5,025	1,362	31	2,043	66	10	0.7	11.32	11.7	0.06

[a]Data are obtained from Regional Statistical Yearbooks.

2.2.1. Atmospheric Nitrogen Deposition

Atmospheric nitrogen deposition includes both wet and dry depositions. Wet deposition of nitrogen was calculated as the ratio of nitrogen deposition to emission (Figure S1 in the supporting information) in each subcatchment [*Ti and Yan*, 2010; *Ti et al*., 2012]. Here we considered only the oxidized form (NO_x), assuming that most of the ammonia or ammonium emission from a watershed is redeposited on the same watershed [*Howarth et al*., 1996]. The NO_x emission data from the years 1980 to 2005 were obtained from the Regional Emission inventory in Asia (REAS version 1.1) with a 0.5° × 0.5° spatial resolution [*Yamaji et al*., 2004; *Ohara et al*., 2007]. The annual N emission in each subcatchment was calculated by multiplying the proportion of the subcatchment within each grid and the REAS emission value for the corresponding grid and aggregating them for each subcatchment [*Hong et al*., 2011b]. Because the data on NO_x emissions for the years 2010–2012 were limited, NO_x emissions for these years were estimated as the energy consumption (Table S1) multiplied by emission factors (Table S2) [*Kato and Akimoto*, 1992], which were also applied in REAS [*Streets and Waldhoff*, 2000; *Ohara et al*., 2007]. In contrast, dry deposition of nitrogen was quantified by a dry/wet deposition ratio [*Anderson and Downing*, 2006; *Jiang et al*., 2012; *Ti et al*., 2012], since the observational data on dry deposition were limited in the Yangtze River basin. In this study, a dry/wet deposition ratio of 3:7 was assumed to calculate the dry deposition rate from that of wet deposition in each subcatchment based on the observed dry and wet deposition rates in Eastern China [*Lü and Tian*, 2007; *Yang et al*., 2010; *Ti et al*., 2012].

2.2.2. Fertilizer Nitrogen Application

The nitrogen input from fertilizers was estimated based on the application amounts of fertilizers and the nitrogen content in the corresponding fertilizers. The application amounts of fertilizer nitrogen were obtained directly from Regional Statistical Yearbooks (Table S3). The nitrogen content in different fertilizers was assumed to be 82.3% in anhydrous ammonia, 46% in urea, 35% in ammonium nitrate, 17% in ammonia bicarbonate, and 12.8% in other combined fertilizers [*Liang*, 1999; *Han et al*., 2014].

2.2.3. Net Food and Feed Nitrogen Import

Net food and feed nitrogen import refers to the mass balance in nitrogen production by creatures and crops against the nitrogen output of consumption by humans and animals. It can be quantified as the net nitrogen import from food and feed = human consumption + animal consumption—crop production for animal consumption—crop production for human consumption—animal production for human consumption [*Jordan and Weller*, 1996]. Here positive and negative values represent the import and export of nitrogen in food and feed, respectively. Animal manure and human waste were eliminated in the estimation of anthropogenic nitrogen inputs to avoid double counting during nitrogen transfers in agricultural products [*Boyer et al*., 2002].

Human nitrogen consumption in food was estimated by multiplying the number of inhabitants (Tables S4 and S5) in urban and rural areas by the annual per capita nitrogen consumption rates (Table S6), which were assessed in the per capita protein consumption at the national urban and rural levels [*Zhai et al*., 2005] and then multiplied by 0.16 (factor of nitrogen in protein) [*European Food Safety Authority*, 2012].

The net nitrogen transport in feed production was calculated using the inventory number of animal species multiplied by the corresponding nitrogen intake (consumption) and excretion (waste production) rates [*Boyer et al*., 2002]. The inventory data were obtained from Regional Statistical Yearbooks (Table S7), while the rates of nitrogen intake and excretion in our nitrogen budgets were obtained from previous studies (Table S8) [*Van Horn*, 1998; *Boyer et al*., 2002; *Han et al*., 2014]. Animal nitrogen production referring mainly to milk, meat, and eggs equaled the difference between intake and excretion. A loss of animal nitrogen product of approximately 10% was assumed as spoilage and inedible components for consumption [*Hong et al*., 2011a; *Han et al*., 2014].

Crop (plus vegetable) nitrogen production was determined by multiplying crop and vegetable yields (Table S9) by their respective N contents (Table S10) [*Wang*, 2003]. Considering that nitrogen contents vary slightly in different kinds of vegetables (approximately 2.08–3.36 g N kg^{-1}) [*Wang*, 2003], an average value (approximately 2.72 g N kg^{-1}) was adopted to represent the nitrogen content in the vegetables grown in the Yangtze River basin [*Han et al*., 2014]. Additionally, it was assumed that there was a loss of crop production of approximately 10% to spoilage [*Hong et al*., 2011a; *Han et al*., 2014].

2.2.4. Agricultural Nitrogen Fixation

The crops grown in the Yangtze River basin mainly include soybeans, rice, peanuts, corn, wheat, and broomcorn. The planted area of each crop was obtained directly from Regional Statistical Yearbooks (Table S11). Additionally, the average values of nitrogen fixed per area were estimated at 9600 kg N km^{-2} yr^{-1} for soybeans, 8000 kg N km^{-2} yr^{-1} for peanuts, 3000 kg N km^{-2} yr^{-1} for rice, and 1500 kg N km^{-2} yr^{-1} for other agricultural land [*Boyer et al*., 2002]. Thus, agricultural nitrogen fixation was quantified on the basis of the nitrogen fixation rate for each crop type multiplied by the sown area of each crop [*Boyer et al*., 2002]. The nitrogen fixation in forests and grass, which are generally considered natural inputs, are not included as components of NANI in this study [*Howarth et al*., 2006].

2.2.5. Uncertainty Analysis

To evaluate the uncertainty in the NANI calculation with corresponding variables, an analysis was performed using a Monte Carlo simulation, which utilized random sampling from predetermined probability distribution functions for the input parameters [*Hammonds et al*., 1994; *Jiang et al*., 2013; *Huang et al*., 2014]. In performing the Monte Carlo simulation in this study, all the parameters used in the NANI estimation were assumed to follow a normal distribution with a coefficient of variation (CV) of 30%, which has been widely applied in watershed N budgeting studies [*Yan et al*., 2011; *Ti et al*., 2012; *Sobota et al*., 2013; *Chen et al*., 2014; *Huang et al*., 2014]. The NANI estimation procedure was formulated in Microsoft Excel embedded with Crystal Ball which was used to define and run the Monte Carlo simulation with 10,000 iterations to obtain the mean and the 95% confidence interval for the annual NANI value of each subcatchment.

2.3. Calculation of Riverine DIN Export

In this study, the Datong hydrological station (117°11′E and 30°46′N; Figure 1) was chosen to estimate the riverine DIN export from the Yangtze River basin, since the station is at the end of the tidal effects from the East China Sea and has long-term measurements of streamflow and water quality. Based on the water discharge and riverine concentrations of DIN (sum of ammonium, nitrate, and nitrite) at the Datong station, the annual riverine DIN export into the Yangtze estuarine and coastal area was quantified as follows:

$$Y = 10^7 \times Q \times C \times A^{-1} \quad (1)$$

where Y denotes the riverine DIN export (kg N km^{-2} yr^{-1}), 10^7 is a conversion factor, Q denotes the water discharge (10^{10} m^3 yr^{-1}), C denotes the annual average DIN concentration (mg N L^{-1}), and A is the basin area (km^2). The data on the annual water discharge estimated from the daily measured water discharge at the Datong station were collected from the Sediment Bulletin of the Yangtze River. The annual average DIN concentration was provided by our colleagues [*Li et al*., 2007; *Dai et al*., 2011; *Xu et al*., 2013], which was estimated from one to three concentration measurements per month and weighted by water discharge. To rationally quantify the link between NANI and riverine DIN yields in the Yangtze River basin, the four components of NANI in the subcatchments below the Datong station were excluded in fitting the relationship between riverine DIN export and NANI.

2.4. Data Analysis

Based on the atmospheric nitrogen deposition, nitrogen fertilizer use, net food and feed nitrogen import, and agricultural nitrogen fixation, the NANI in each subcatchment was quantified by summing the values of these nitrogen sources. A one-way analysis of variance (ANOVA) was conducted to examine the temporal and spatial differences in NANI across the Yangtze River basin. A grey relational grade analysis was performed between NANI and socioeconomic factors (Table S12) with a discrimination coefficient of 0.5 [*Han et al*., 2014]. A simple exponential or linear regression was performed to determine the relationship between NANI and the riverine nitrogen export. However, previous studies have shown that the influence of NANI combined with water discharge on the riverine DIN export is best described using a power function [*Caraco and Cole*, 1999; *McIsaac et al*., 2001; *Han et al*., 2009; *Huang et al*., 2014]; thus, in the present work, the following model developed by *Caraco and Cole* [1999] was used to examine the integrated effects of NANI and water discharge on the riverine DIN export:

$$Y = a \times Q^b \times \exp(c \times \text{NANI}) \quad (2)$$

where Y is the riverine DIN export (kg N km^{-2} yr^{-1}), Q is the annual water discharge (10^{10} m^3 yr^{-1}), and a, b, and c are unknown parameters estimated by regression.

3. Results and Discussion

3.1. Spatial and Temporal Variations of NANI

The geographic distribution of NANI across the Yangtze River basin was characterized by a gradual increase from the western to eastern subcatchments (Figure 2 and Table S13). To examine the spatial differences in

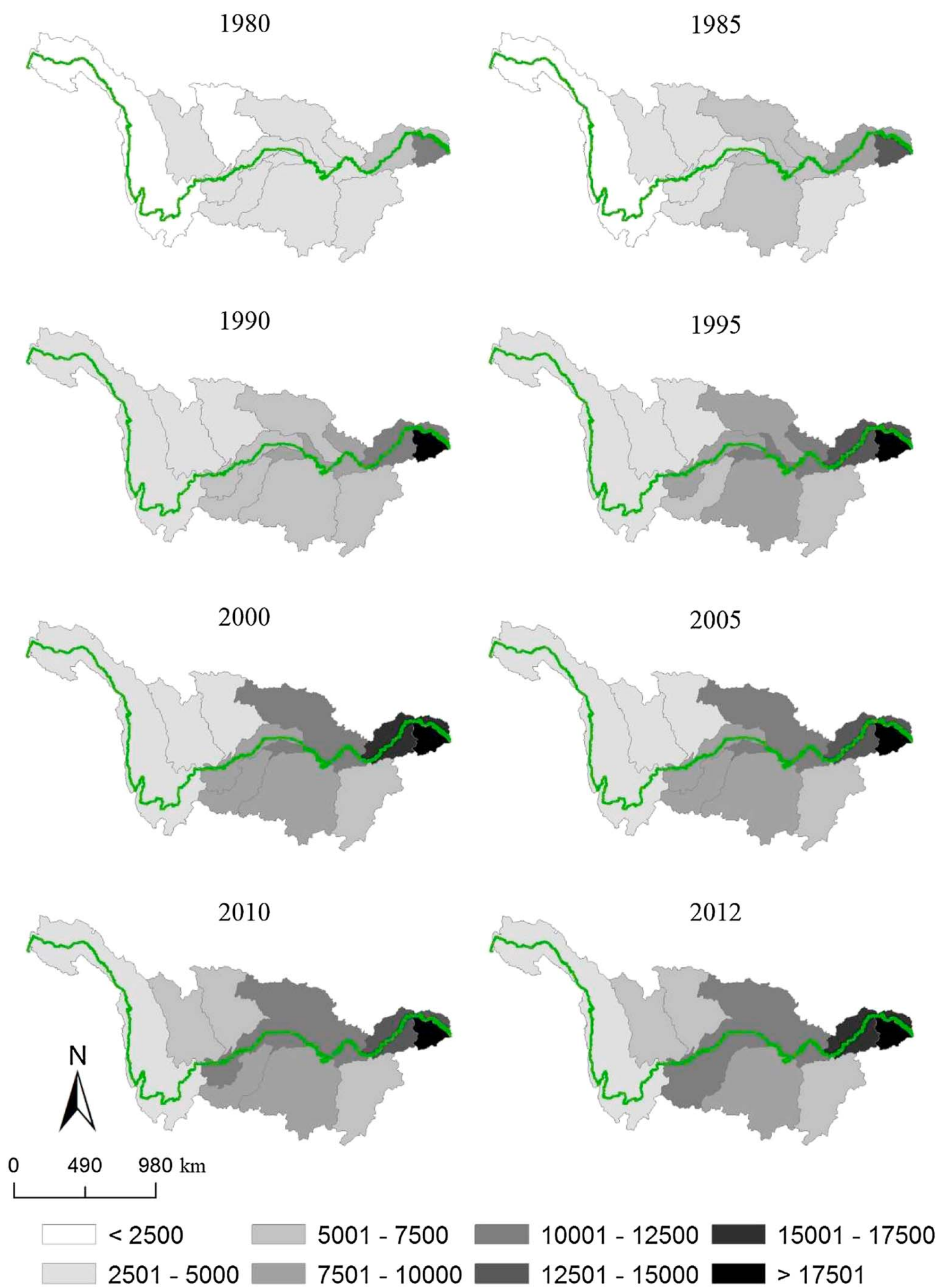

Figure 2. NANI (kg N km^{-2} yr^{-1}) in different subcatchments of the Yangtze River basin presented in a GIS map.

NANI, the multiannual (1980–2012) average NANI in each subcatchment is also quantified (Figure 3). A significant spatial variation in the multiannual average NANI was observed (one-way ANOVA, $p < 0.01$), suggesting that the trajectory in NANI differed between subcatchments. The greatest NANI was recorded in the TH subcatchment (18,574.6 ± 3753.7 kg N km^{-2} yr^{-1}), followed by the LM subcatchment (12,805.5 ± 2575.4 kg N km^{-2} yr^{-1}). However, the lowest NANI appeared in the JSJ subcatchment (3054.1 ± 537.1 kg N km^{-2} yr^{-1}). The observed spatial difference in NANI across the Yangtze River basin was attributed mainly to the uneven distribution of the population and an imbalance in the economic development among subcatchments (Tables 1 and S12). In addition, NANI in most subcatchments of the Yangtze River basin is relatively high compared with other basins in the world (one-way ANOVA, $p < 0.01$; Figure 3). For example, NANI varied from 2700 to 4900 kg N km^{-2} yr^{-1} in

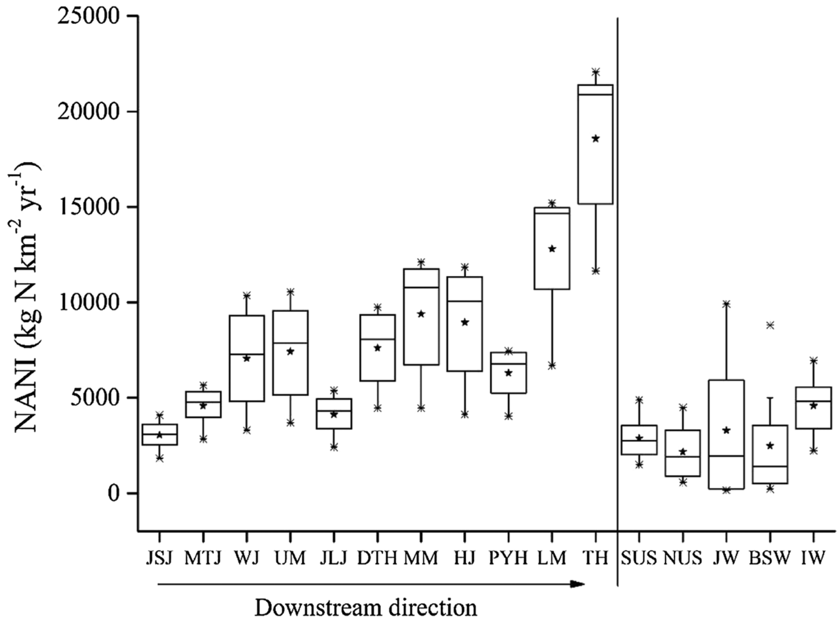

Figure 3. Multiannual (1980–2012) average NANI in subcatchments of the Yangtze River basin and comparison with other basins in the world. SUS, NUS, JW, BSW, and IW denote southeastern US watersheds, northeastern US watersheds, Japanese watersheds, Baltic Sea watersheds, and Indian watersheds, respectively. Horizontal lines indicate the median, five-point stars show the mean, asterisks indicate outliers, the boxes give the 25th and 75th percentiles, and whiskers show the range from the 5th to 95th percentiles. The arrow indicates the downstream direction.

southeastern U.S. watersheds [*Schaefer and Alber*, 2007], from 560 to 4500 kg N km^{-2} yr^{-1} in northeastern U.S. watersheds [*Hong et al.*, 2011a], from 160 to 9930 kg N km^{-2} yr^{-1} in Japanese watersheds [*Hayakawa et al.*, 2009], from 300 to 8800 kg N km^{-2} yr^{-1} in Baltic Sea watersheds [*Billen et al.*, 2011], and from 2223 to 6955 kg N km^{-2} yr^{-1} in Indian watersheds [*Swaney et al.*, 2015].

Significant temporal changes in NANI were observed in the Yangtze River basin (one-way ANOVA, $p < 0.01$). The total NANI in the entire basin increased from 3537.0 ± 615.3 kg N km^{-2} yr^{-1} in 1980 to 8176.6 ± 1442.1 kg N km^{-2} yr^{-1} in 2012 (Figure 4). The greatest increase in NANI occurred between 1980 and 1995, during which time NANI increased by approximately 94% (3537.0 ± 615.3 to 6877.9 ± 1298.5 kg N km^{-2} yr^{-1}). After that, it showed a relatively slow increase. During the 2000–2012 period, it increased by approximately 17% (6965.3 ± 1277.3 to 8176.6 ± 1442.1 kg N km^{-2} yr^{-1}). A grey relational grade analysis showed that fertilizer use and the population amount and density were the primary factors responsible for the changes in NANI across the Yangtze River basin. Among the social factors (total population, total population density, and rural population density), the total population density had the greatest relational grade (0.973), indicating that the total population density was the primary social factor in relation to the changes in NANI. The cultivated land area, total crop yield, and fertilizer use were the main agricultural factors, and their relational grades were 0.895, 0.897, and 0.962, respectively. The total fertilizer use had the greatest relational grade, indicating that among the agricultural factors, the total fertilizer use was the main factor determining the changes in NANI. Gross domestic product and gross agricultural and industrial outputs were the main economic factors, and their relational grades were 0.843, 0.857, and 0.819, respectively. The total agricultural output had the greatest relational grade, indicating that the total agricultural output was the main economic factor reflecting the changes in NANI in the Yangtze River basin.

3.2. Contributions of Nitrogen Sources to NANI

The contributions of different sources to NANI in the Yangtze River basin were quantified (Figure 5 and Table S14). The application of nitrogenous fertilizer was always the predominant source to NANI, which contributed 40.8–56.1% of NANI. Over the 1980–2012 period, nitrogen fertilizer use in the Yangtze River basin increased from 1444.0 ± 151.6 to 4153.6 ± 424.8 kg N km^{-2} yr^{-1} (Figure 5). The largest inputs of fertilizer

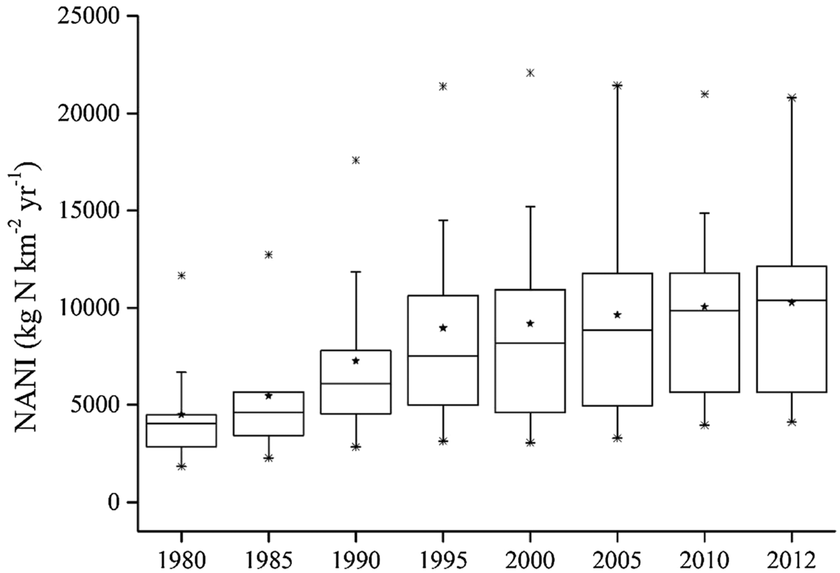

Figure 4. Temporal variations of total NANI in the Yangtze River basin from the years 1980 to 2012. Horizontal lines indicate the median, five-point stars show the mean, asterisks indicate outliers, the boxes give the 25th and 75th percentiles, and whiskers show range from the 5th to 95th percentiles.

nitrogen appeared in the TH subcatchment, with values of 7824.5 ± 1437.8–14,275.1 ± 2770.0 kg N km^{-2} yr^{-1}, while the smallest inputs of fertilizer nitrogen occurred in the JSJ subcatchment, with values of 474.0 ± 124.9–1629.8 ± 346.1 kg N km^{-2} yr^{-1} (Figure S2). The proportions of net nitrogen in food and feed dropped dramatically from 37.6% to 18.3% between 1980 and 2012 (Table S14). The net nitrogen import from food and feed varied from 1329.8 ± 134.1 to 1884.7 ± 201.5 kg N km^{-2} yr^{-1} in the entire basin (Figure 5). A relatively high net nitrogen import from food and feed was observed in the WJ subcatchment, while relatively low net nitrogen imports from food and feed were detected in the TH and JLJ subcatchments (Figure S3). The contributions of agricultural nitrogen fixation decreased from 15.3% in 1980 to 7.4% in 2012 (Table S14). In the entire basin, agricultural nitrogen fixation varied between 536.3 ± 55.1 and 604.7 ± 62.0 kg N km^{-2} yr^{-1} from 1980 to

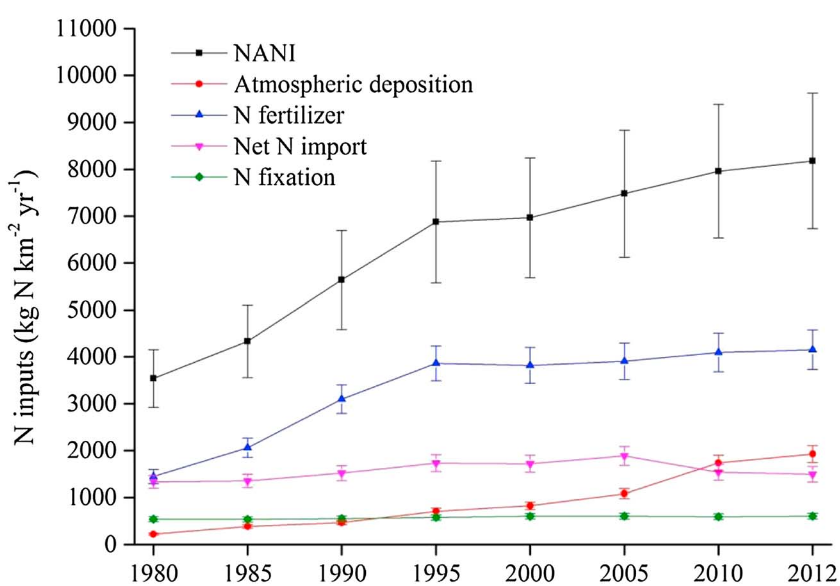

Figure 5. Total NANI in the Yangtze River basin from the years 1980 to 2012. The error bar denotes the 95% confidence interval of nitrogen inputs.

Table 2. Regression Analyses Between Riverine DIN Export (Y, kg N km^{-2} yr^{-1}) and Individual Factors (x) in the Yangtze River Basin During the 1980–2012 Period

Independent Variables	Formulas	R^2	p
NANI (kg N km^{-2} yr^{-1})	$Y = 311.46\exp(0.0002x)$	0.68	<0.01
	$Y = 0.164x + 74.887$	0.59	<0.01
Nitrogenous fertilizer (kg N km^{-2} yr^{-1})	$Y = 352.19\exp(0.0003x)$	0.77	<0.01
Net N in food and feed (kg N km^{-2} yr^{-1})	$Y = 1.3753x - 1064.1$	0.59	<0.01
Agricultural fixation (kg N km^{-2} yr^{-1})	$Y = 9.4045x - 4138.2$	0.69	<0.01
Annual water discharge (10^{10} m^3 yr^{-1})	$Y = (3 \times 10^{-5})x^{3.8714}$	0.64	<0.01

2012 (Figure 5). Over the 32 years, the maximal and minimal rates of agricultural nitrogen fixation appeared in the LM and JSJ subcatchments, respectively (Figure S4). The contribution of atmospheric nitrogen deposition to NANI increased from 6.3% to 23.5% during the 1980–2012 period (Table S14). Relatively high rates of atmospheric nitrogen deposition occurred in the LM and TH subcatchments (Figure S5). In contrast, relatively low rates of atmospheric nitrogen deposition occurred in the JSJ subcatchment. In general, with the industrial development in the Yangtze River basin, a large number of chemical plants and factories have arisen and accelerated nitrogen emissions [*Tian et al.*, 2001; *Lü and Tian*, 2007]. Therefore, atmospheric deposition has made an increasing contribution to NANI and become the second largest component in the nitrogen budgets of recent years.

3.3. Relationships Between NANI and Riverine DIN Export

The riverine DIN flux is tightly linked to human activities and has been found to be significantly correlated with NANI in previous studies [*McIsaac et al.*, 2001, 2002; *Han and Allan*, 2008; *Howarth et al.*, 2012; *Swaney et al.*, 2012]. In the present work, the relationship was slightly better predicted by using an exponential ($R^2 = 0.68$, $p < 0.01$) rather than a linear model ($R^2 = 0.59$, $p < 0.01$) (Table 2). The riverine DIN export was also significantly correlated with chemical nitrogen fertilizer use, net food and feed nitrogen input, and agricultural nitrogen fixation (Table 2), while it was not closely correlated with atmospheric nitrogen deposition ($p > 0.05$). The chemical nitrogen fertilizer use had the largest portion of variability (77%) in the annual riverine DIN fluxes (Table 2). The high dependence of annual riverine DIN yield on nitrogen fertilizer was likely due to the increasing application of chemical nitrogen fertilizer on agricultural land, because nitrogen fertilizers mainly in an inorganic form may be easily flushed into surface waters with rainfall-runoff [*McIsaac et al.*, 2002; *Hong et al.*, 2013]. Furthermore, it showed that the riverine DIN yield was significantly correlated with annual water discharge (Table 2). Hence, the correlation between annual discharge and riverine DIN export is of concern when it is used as a predictive variable to describe the effect of the climate on the fraction of nitrogen exported from watersheds [*Howarth et al.*, 2012].

In this study, the integrated influence of NANI and water discharge on the riverine DIN export was analyzed using equation (2). With the data obtained from the present work, we had a specific equation for the Yangtze River basin:

$$Y = 0.002 \times Q^{2.72} \times \exp\left(1.4 \times 10^{-4} \times \mathrm{NANI}\right) \tag{3}$$

Equation (3) accounted for 90% of the variation in annual DIN yields over the study period (Table 3). This model result showed that the combined effect of NANI and water discharge can better explain the interannual changes of riverine DIN export from the Yangtze River basin, compared to individual variables. Additionally, it was confirmed that the model can be applied to predict annual riverine DIN export in response to anthropogenic N inputs and climate changes of the study area. However, the annual riverine DIN export may be affected by the construction of the Three Gorges Dam on the Yangtze River. For instance, the impoundment of water above the dam can foster denitrification [*Zhang et al.*, 1999; *David et al.*, 2006; *Yuan et al.*, 2012], and thus decrease the riverine DIN export. In addition, the seasonal exports of NANI may

Table 3. Regression Model for Riverine DIN Export as an Exponential Function of NANI and a Power Function of Water Discharge

Parameters	Values	p	Lower 95%	Upper 95%	Significance F	R^2
a	0.002	<0.05	4.3×10^{-6}	0.95	0.001	0.90
b	2.72	<0.05	1.32	4.12		
c	0.00014	<0.05	7.4×10^{-5}	2.1×10^{-4}		

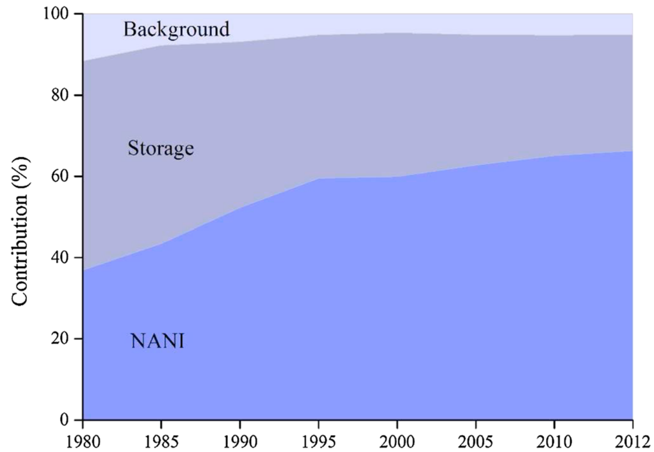

Figure 6. Contributions of the current year's NANI, watershed nitrogen storage, and natural background nitrogen sources to the annual riverine DIN export from the Yangtze River basin between 1980 and 2012.

vary following the dam construction. It has been reported that the operating strategy for the Three Gorges Dam that stores part of the high flows in the summer to maintain hydroelectric power generation in the winter (the low flow season) changes the seasonal distribution of water flow [*Yuan et al.*, 2012]. Therefore, the construction and operation of the Three Gorges Dam would mediate the seasonal changes in riverine DIN fluxes by controlling the seasonal variations in water discharge.

3.4. Riverine DIN Sources Apportionment

In numerous studies [*Howarth*, 2008; *Han et al.*, 2009; *Howarth et al.*, 2012; *Swaney et al.*, 2012], riverine nitrogen sources were generally apportioned to NANI and natural background sources (i.e., predicted exports when NANI = 0). However, it has also been documented that a considerable fraction of NANI can be temporally retained in watersheds [*Howarth et al.*, 2012; *Swaney et al.*, 2012] and subsequently released to rivers in following years [*Stålnacke et al.*, 2003; *Chen et al.*, 2014]. Equation (3) developed here also showed the effect of stored NANI on annual riverine DIN export. In this study, riverine DIN export was thus apportioned to the current year's NANI (Y_{NANI}), stored nitrogen (Y_S), and natural background nitrogen (Y_B) [*Huang et al.*, 2014]. When NANI was set equal to 0, it represented the amount of DIN that originated from Y_S and Y_B:

$$Y_S + Y_B = 0.002 \times Q^{2.72} \quad (4)$$

The DIN export from the current year's NANI was then quantified as:

$$Y_{NANI} = 0.002 \times Q^{2.72} \times \exp\left(1.4 \times 10^{-4} \times \text{NANI}\right) - 0.002 \times Q^{2.72} \quad (5)$$

To distinguish Y_S and Y_B, we assumed that the annual natural background (Y_B) was the water discharge multiplied by the average background DIN concentration (C_B) observed in primitive rivers [*Meybeck*, 1982; *Huang et al.*, 2014]. Then, Y_S can be estimated as

$$Y_S = 0.002 \times Q^{2.72} - 10^7 \times Q \times C_B \times A^{-1} \quad (6)$$

where C_B is generally estimated at 0.12 mg N L^{-1} [*Meybeck*, 1982; *Huang et al.*, 2014]. To evaluate the uncertainty, a 30% coefficient of variation (CV) was assumed for C_B (i.e., 95% confidence interval: 0.08–0.16 mg N L^{-1}) and used for a total of 10,000 Monte Carlo simulations to obtain annual Y_S values. In the Yangtze River basin, the riverine DIN export from the current year's NANI was estimated at 164–863 kg N km^{-2} yr^{-1} (average: 595 kg N km^{-2} yr^{-1}). The current year's NANI contributed 37–66% (average: 56%) of the riverine DIN export (Figure 6). The large proportion shows that the current year's NANI is an essential contributor to the riverine DIN yield. The natural background sources contributed 5–12% (average: 6%) of the riverine DIN export (Figure 6). This DIN export from the natural background was estimated at 52–67 kg N km^{-2} yr^{-1} (average: 60 kg N km^{-2} yr^{-1}), which is comparable to the value (58–278 kg N km^{-2} yr^{-1}) from previous studies [*Han et al.*, 2009; *Howarth et al.*, 2012; *Huang et al.*, 2014]. In addition, the riverine DIN yield from storage sources was estimated at 229–510 kg N km^{-2} yr^{-1} (average: 367 kg N km^{-2} yr^{-1}). The stored NANI contributed 29–51% of the DIN export (Figure 6), which is similar to results (15–76%) from previous studies [*Van Breemen et al.*, 2002; *Huang et al.*, 2014]. The stored NANI likely originated from mineralization of soil organic nitrogen [*Van Breemen et al.*, 2002; *Booth et al.*, 2005; *Kopáček et al.*, 2013] and/or the nitrogen export from groundwater [*Iqbal*, 2002; *Van Breemen et al.*, 2002; *Howden et al.*, 2010]. Considering the timescales for soil nitrogen mineralization and hydrologic processes, the stored NANI effect could continue for years to decades [*Booth et al.*, 2005; *David et al.*, 2010; *Howden et al.*, 2010; *Swaney et al.*, 2012; *Huang et al.*, 2014]. However, the construction and operation of the Three Gorges Dam will significantly change the hydrologic process of the Yangtze River [*Yuan et al.*, 2012], consequently affecting the export of stored NANI.

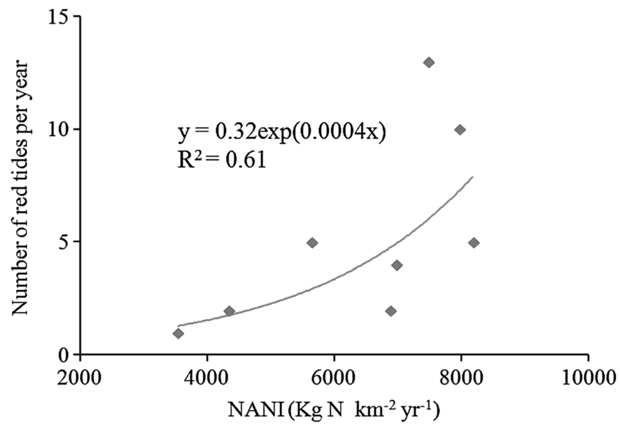

Figure 7. Correlation between NANI and the number of red tides occurring in the Yangtze River estuary and the adjacent area over the 1980–2012 period.

Therefore, more research work is needed to identify the storage effect on the nitrogen budget and export in the Yangtze River basin.

3.5. Impacts of NANI on Red Tide Occurrence

The occurrence of red tides has become a common phenomenon in the Yangtze estuary and the adjacent coastal area in recent decades. With the recorded data on red tides [*Wang*, 2006; *Liu et al.*, 2011; *Strokal et al.*, 2014], the relationship between NANI and the frequency of red tide occurrences was quantified in the present study. A power function correlation ($R^2 = 0.61$, $p < 0.01$) was observed between NANI and the red tide occurrence frequency (Figure 7). This relationship implies that NANI in the Yangtze River basin contributed significantly to the occurrence of red tides [*Chai et al.*, 2006; *Li et al.*, 2007; *Li et al.*, 2014]. This study also highlights the importance of controlling NANI in the Yangtze River basin for protecting the ecoenvironmental health of the estuarine and coastal ecosystem. Interestingly, the seasonal control of riverine DIN exports by the Three Gorges Dam may help decrease the occurrence of red tides in warm (flood) seasons, because the Three Gorges Dam can reduce the water flow and associated DIN exports into the estuarine and coastal zone in these seasons.

3.6. Forecasting Future Riverine NANI and DIN Export

To predict future NANI and riverine DIN export for the period 2013–2030 using equation (3), the average NANI (7645.3 kg N km^{-2} yr^{-1}) and water discharge (9.21×10^{11} m^3 yr^{-1}) from 2000 to 2012 were used as the baseline (current) conditions. We forecasted possible future trends of NANI and riverine DIN export based on the following three scenarios.

Scenario 1: "Status Quo." This scenario projects a 75% increase of NANI in the Yangtze River basin from the baseline to 13,357.1 kg N km^{-2} yr^{-1} in 2030. This increase results mainly from enhanced fertilizer application (3% increase per year as in the past years) in agriculture to further increase crop yields and atmospheric NO_x deposition (6% increase per year as in the past years) due to the increasing fuel consumption for vehicles and electricity production. The enhanced net nitrogen import in food and feed (1% increase per year as in the past years) contributes 5.7% of the NANI increase, due to increased human and livestock populations. Assuming that water discharge remains constant, riverine DIN export in 2030 would increase by approximately 122% from the baseline (1285.8 kg N km^{-2} yr^{-1} to 2860.6 kg N km^{-2} yr^{-1}; Figure S6) due to a 75% increase in NANI from 2013 to 2030.

Scenario 2: "tackling." Under the tackling scenario, NANI would be approximately 21% less than the baseline (Figure S6). This decrease may partly result from decreased fertilizer use (2% decrease per year) and agricultural nitrogen fixation (1% decrease per year) by improving the fertilizer-use efficiency, developing ecological agriculture and modifying crop breeds [*Peng et al.*, 2002; *Chen et al.*, 2014]. Considering the increased demand for nitrogen by humans and livestock, a reduction in the net nitrogen export in food and feed (1% decrease per year) is expected [*Chen et al.*, 2014], which contributes to a decrease in NANI of approximately 17%. The atmospheric NO_x deposition is assumed to decrease by 0.1%/year through controlling NO_x emissions from industrial and traffic sources and adjusting the structure of energy consumption [*Ohara et al.*, 2007], which can contribute to an approximate 2% decrease in NANI. This scenario suggests that the riverine DIN export would decrease by approximately 20% in 2030, given no change in water discharge.

Scenario 3: "climate change." This scenario reflects the potential effects of future climate changes on anthropogenic nitrogen inputs and riverine DIN export in the Yangtze River basin. Under scenarios developed by the Intergovernmental Panel on Climate Change (IPCC) Special Report on Emissions Scenarios, the water discharge is assumed to decrease by approximately 1.28%, while temperature would rise by 0.2–1°C as a result of the increase in atmospheric CO_2 in the Yangtze River basin for the next two decades [*IPCC*, 2007; *Zhang et al*., 2014]. Climate change has the potential to exert a strong influence on the productivity of symbiotic N_2-fixing organisms and the amounts of nitrogen contributed by these organisms to agroecosystems [*Howarth et al*., 2006; *Thomas et al*., 2007; *Daniel et al*., 2009; *Shi et al*., 2015]. Due to the effects of climate change, agricultural nitrogen fixation is assumed to have a 50% increase by 2030 [*Thomas et al*., 2007; *Daniel et al*., 2009]. However, the decrease in nitrogen fertilizer use efficiency partly caused by the negative consequences of climate change may lead to an approximately 5% increase in the demand of fertilizer by 2030 [*Van Essen*, 2008; *Zhang et al*., 2015]. Furthermore, it is predicted that there is an approximately 10% increase in atmospheric NO_x deposition by 2030, mainly because more energy would be consumed in a warmer climate [*Wilbanks et al*., 2008; *Karl*, 2009]. In addition, considering the increase in crops yield stimulated by the CO_2-fertilzation effect, an approximately 5% reduction in net nitrogen export in food and feed is expected by 2030 [*Daniel et al*., 2009; *Shi et al*., 2015]. Under all of these conditions, this scenario projects an increase of 7.3% for NANI and 4.8% for riverine DIN export in the Yangtze River basin by 2030 (Figure S6).

Although these predictions are subject to uncertainties in anthropogenic nitrogen inputs and climate change, these predicted results roughly reflect the potential effects of human activities and climate change on riverine DIN export from the Yangtze River basin. The response of the riverine DIN yield can provide a reference for adopting and assessing relevant watershed nitrogen management strategies.

4. Conclusion

This study presents a historically explicit analysis of anthropogenic nitrogen inputs in the Yangtze River basin and associated relationships with riverine DIN export. Over the past three decades, the NANI has increased from 3537.0 ± 615.3 kg N km^{-2} yr^{-1} in 1980 to 8176.6 ± 1442.1 kg N km^{-2} yr^{-1} in 2012. The dominant NANI source was from chemical fertilizer applications with an average contribution of 51.1%. Based on the regression model of the riverine DIN yield that incorporated NANI and water discharge variables, the annual NANI, catchment nitrogen storage, and natural background sources were determined to account for 56%, 38%, and 6% of the annual riverine DIN export, respectively. The annual riverine DIN export predicted in 2030 would increase by approximately 122% under the status quo scenario, while it would decrease by approximately 20% under the tackling scenario if some management practices work in the coming years. Under the climate change scenario, the annual riverine DIN export is predicted to have an approximately 4.8% increase by 2030. These results imply that anthropogenic activities and future climate changes have a significant influence on the nitrogen inputs in the basin and the fractional nitrogen exported by river. Therefore, an integrated nitrogen management scheme considering the effects of anthropogenic nitrogen inputs and climate changes is required to assess and optimize watershed nitrogen management measures for protecting the Yangtze estuarine and coastal waters.

Acknowledgments
This work was funded by the National Natural Science Foundations of China (41322002, 41130525, 41271114, and 41071135), the State Key Laboratory of Estuarine and Coastal Research. It was also supported by the Programs for New Century Excellent Talents in University (NCET) and Outstanding academic leaders of Shanghai City. We thank Wayne S. Gardner and anonymous reviewers for constructive comments on earlier versions of the manuscript. Data presented in this paper can be obtained by sending a written request to the corresponding author.

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