

Nitrogen budget and riverine nitrogen output in a rice paddy dominated agricultural watershed in eastern China

Xiaoyuan Yan · Zucong Cai · Rong Yang ·
Chaopu Ti · Yongqiu Xia · Feiyue Li ·
Jianqun Wang · Aijun Ma

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Abstract The nitrogen (N) budget calculation approach is a useful means of evaluating the impact of human activity on the N cycle. Field scale N budget calculations may ignore the interactions between landscapes, and regional scale calculations rely on statistical data and indirect parameters. Watershed scale budget calculations allow for a more direct quantification of N inputs and outputs. We conducted N budget calculations for a rice paddy-dominated agricultural watershed in eastern China for 2007–2009, based on intensive monitoring of stream

N dynamics, atmospheric deposition, ammonia (NH₃) volatilization and household interviews about N-related agricultural activities. The results showed that although total N input to the watershed was up to 280 kg N ha⁻¹ year⁻¹, riverine discharge was only 4.2 kg N ha⁻¹ year⁻¹, accounting for 1.5% of the total N input, and was further reduced to 2.0 kg N ha⁻¹ year⁻¹ after reservoir storage and/or denitrification removal. The low riverine N output was because of the characteristics of the rice paddy-dominated landscape, which intercepts run-off and enhances soil denitrification. The watershed actually purified the N in rainwater, as N concentrations in river discharge were much lower than those in rain water. Major N outputs included food/feed export, NH₃ volatilization from chemical fertilizer and manure, and emissions from crop residue burning. Net reactive gaseous emissions (emissions minus deposition) accounted for 5.5% of the total N input, much higher than riverine discharge. Therefore, the agricultural N cycle in such paddy-dominated watersheds impacts the environment mainly through gas exchange rather than water discharge.

X. Yan (✉) · Z. Cai · R. Yang · C. Ti · Y. Xia · F. Li
State Key Laboratory of Soil and Sustainable Agriculture,
Institute of Soil Science, Chinese Academy of Sciences,
Nanjing 210008, China
e-mail: yanxy@issas.ac.cn

J. Wang
College of Hydrology and Water Resources, Hohai
University, Nanjing 210098, China

A. Ma
Jiangsu Polytechnic College of Agriculture and Forestry,
Jurong 212400, China

Present Address:

F. Li
College of Urban Construction and Environment Science,
Anhui Science and Technology University,
Fengyang 233100, China

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Abbreviations

NANI Net anthropogenic nitrogen input
N Nitrogen
TN Total dissolved nitrogen

Introduction

Reactive nitrogen (N) levels have increased dramatically worldwide due to anthropogenic activities such as over-fertilization, high stocking rates of livestock and increased combustion of fossil fuels (Galloway et al. 2004). Excessive reactive N is considered by some researchers to be the third largest threat to our planet after biodiversity loss and climate change (Giles 2005), as it induces a series of eco-environmental problems such as the greenhouse effect, destruction of the ozone layer, acid rain, nitrate pollution in groundwater, eutrophication of lakes and offshore water, and biodiversity reduction locally, nationally and globally (Vitousek et al. 1997).

Nitrogen fertilizer and N fixing crops are the two main anthropogenic reactive N sources worldwide (Galloway et al. 2004). Nitrogen budget calculations in agricultural systems are therefore useful for developing a quantitative understanding of N sources, assessing overall availability of N to crops, and evaluating the environmental impacts of N cycling. At the field scale, numerous studies have been conducted to measure fluxes of various forms of N. However, due to the large spatial heterogeneity of agricultural systems and the interaction between land uses, watershed studies are necessary to calculate the overall N balances, and to integrate the environmental effects of N cycling. While many calculations for agricultural watersheds have been done in the USA and Europe (e.g., David et al. 1997; Gentry et al. 2009; Lowrance 1992; Ventura et al. 2008), fewer have been done in Asia. Watershed N budgets are greatly affected by land use, climate and hydrology (Schaefer and Alber 2007; Sobota et al. 2009). Rice paddy is a major agricultural land use in the monsoon Asia region where more than 90% of the global rice fields are located (FAO 2008). Rice paddies are usually constructed with a bank and are flooded for most of the growing season and in rice paddy-dominated watersheds, multi-pond systems are common. These characteristics greatly affect N cycle processes (Yan et al. 1998).

The lower reaches of the Yangtze River, located in eastern China, has long been one of the most densely populated agricultural regions and it has a very long history of productive rice-based agriculture (Wu et al. 2009). Anthropogenic reactive N has far exceeded natural biologically fixed N in natural terrestrial

ecosystems in this region (Xing et al. 2002). Fertilizer N application rates are as high as 550–600 kg N ha⁻¹ year⁻¹ for two crops per year (Xing and Zhu 2002). Surface water pollution is increasingly becoming a serious environmental problem and the excessive use of N fertilizer has been blamed as a major contributor (Qin et al. 2007). Field scale studies have been widely conducted to quantify the sources and fate of N (Liang et al. 2007; Tian et al. 2007; Wang et al. 2007; Zhao et al. 2009). However, field scale studies tend to ignore the interaction between fields, especially for paddy-dominated watersheds in China and Southeast Asia where fields are not separately drained but are directly connected. Watershed N budget calculation would allow a more direct quantification of the impact of the agricultural N cycle on surface water and air quality.

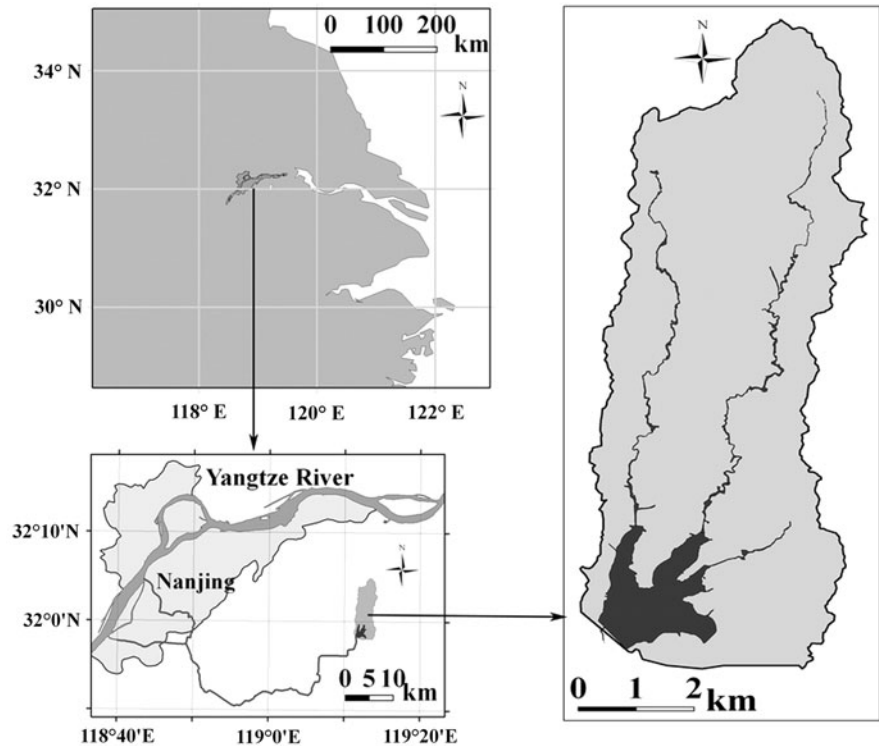
In this study, we present an N budget for a small rice paddy-dominated agricultural watershed in eastern China, with measurements of riverine N output, ammonia (NH₃) volatilization, atmospheric N deposition and crop uptake, and agricultural activity data obtained through household interviews.

Materials and methods

Watershed description

The study was conducted in the Jurong Reservoir watershed, located 40 km southeast of Nanjing, Jiangsu province, China (32°01'N, 119°13'E, Fig. 1). It is one of the headstreams of the Qinhuai River, a small tributary of the Yangtze River. The watershed has a total area of 45.5 km², of which, 32.2% are rice paddies, 22.8% is cultivated upland, 27.5% contains buildings and roads, 9.3% is tea gardens and artificial forest and the rest is occupied by a reservoir, three streams and thousands of small ponds. It has a hilly landscape with elevations ranging from 17.5 to 280 m, but mostly below 50 m. There are no drainage pipes, tile drainage or canals in the watershed and the surface run-off comes from the fields around the streams or some small naturally formed ditches. The croplands are irrigated by pumping water stored in the ponds, streams and reservoir, or through naturally formed ditches. The three streams join the reservoir located at the lowest part of the watershed (Fig. 1). The discharge gate of the reservoir is the only outlet for

Fig. 1 Map and location of Jurong reservoir watershed



the surface water from the watershed, which allows accurate monitoring of the N discharge rate from the watershed.

The annual mean temperature of the study area is 15°C and the annual mean precipitation is 1,050 mm. Typical soils are Anthrosols (rice paddy) and Ferric/Haplic Luvisols (upland) (FAO classification). Soil organic carbon contents range from 12.1 to 21.9 g kg⁻¹ and total N from 0.75 to 1.22 g kg⁻¹. There is no industry or intensive livestock farming in the watershed. Therefore, agriculture is the dominant local source of N contamination. Rice–wheat and maize–oil rape are the major annual cropping rotations for the paddy fields and upland fields, respectively. In the residential area, there is a small number of livestock raised for consumption. Human and livestock waste is applied to farmlands after being treated in the open air in the residential area for a few months. No human and livestock waste is directly discharged to water bodies.

Nitrogen budget model

Nitrogen inputs to the watershed include chemical fertilizer, atmospheric deposition, biological N fixation, and food/feed imports. Nitrogen outputs include food/

feed export, biomass burning emission of N gases, NH₃ volatilization from chemical fertilizer and human/animal waste, riverine discharge, and in-stream denitrification. Reliable techniques for determining field denitrification were not available (Groffman et al. 2006). Nitrogen leaching to ground water is difficult to quantify at a watershed scale, but field studies conducted in surrounding regions have shown that it was minimal (Zhu and Chen 2002). We therefore omitted N leaching and assumed that the difference between N inputs and outputs was due to soil storage and denitrification.

Household interviews of N related agricultural activities

About 600 households, representing approximately 10% of the total households in the watershed, were interviewed in 2007 and 2008. Contents of the interview included N related activity data such as cultivation area and type of crops, fertilization rate, crop yield, fate of crop residues, livestock population, management of human and livestock excreta, and food/feed import and export. The total number of households in the watershed was obtained from the local statistical office.

Atmospheric N deposition

Wet deposition was measured by collecting rainfall samples using two rain gauges installed approximately 1.5 m from the ground at a crop field site and a residential site in the watershed. After each rain event, all collected rainwater was thoroughly mixed, and an aliquot was placed in a plastic bottle and immediately frozen at -20°C until analysis.

Dry deposition was calculated as the product of the air concentrations of NO_2 and NH_3 and modeled deposition velocity. Nineteen Ogawa samplers (Ogawa & Co., USA) were deployed to various places in the watershed approximately 1.5 m from the ground to capture gaseous NO_2 and NH_3 . Air concentrations of NO_2 and NH_3 were then calculated according to Ogawa sampling protocol for NO_2 and NH_3 (Sampling Protocol Using the Ogawa Sampler, February, 1998). Deposition velocity was calculated by using a meteorological model (details of the calculation are available at Su et al. (2009)). An automatic weather station (Vantage Pro Plus, Davis Instrument Crop., San Francisco, CA, USA) was installed in the watershed to monitor meteorological parameters needed for the calculation of deposition velocity.

Chemical N fertilizer input and biological N fixation

Total chemical fertilizer N input was estimated from the cultivation area and the N application rate of each crop obtained from the household interviews. Biological N fixation was estimated for different crops on an area basis. Based on field measurements, Zhu (1997) estimated that in Chinese agro-ecosystems, soybean fixes N at 64 kg N ha^{-1} , and rice paddy fixes N at 45 kg N ha^{-1} . We used these rates to estimate N fixation by soybean and rice paddies in the watershed. Local data for N fixing by other upland crops are not available (Zhu 1997); we therefore used a default value of 15 kg N ha^{-1} (Burns and Hardy 1975).

NH_3 volatilization from chemical N fertilizer and human/livestock excreta

Ammonia volatilization from applied N fertilizer was measured on three paddy fields and three upland fields using the method described by Dong et al. (2006). Since the paddy fields were cropped with rice

in summer and wheat in winter, and the uplands were cropped with maize in summer and oil rape in winter, NH_3 emission factors were available for these four major crops. Soybean and cotton are planted also in summer and on upland, thus the emission factor for maize was used as a default.

Ammonia is emitted from human and livestock excreta in two stages, during the storage period and after being applied to the fields as fertilizer (IPCC 2007). The total emission is determined from the N excreta rate per person or animal, the NH_3 emission rates during storage and after the excreta has been applied to the field. The calculation method followed the IPCC (2007) approach and Xing and Yan (1999).

Dissolved N concentrations and N discharge into and out of the reservoirs

Water samples from five ponds and 14 sites along the three streams were collected biweekly, and from the discharge gate of the reservoir daily or on discharge days (discharge from the reservoir was manually controlled). Water samples were placed in clean plastic bottles, and immediately frozen at -20°C until analysis for NH_4^+ , NO_3^- , and total dissolved N (TN) using a flow injection analyzer (Skalar, Netherlands). The samples were filtered before analysis.

Daily water discharge into the reservoir was calculated from the monitored water volume of the reservoir, gate discharge out of the reservoir, and precipitation onto the reservoir. The N discharges into and out of the reservoir were determined by multiplying N concentrations and the discharge volumes of water.

Sediment storage and denitrification

Nitrogen storage and removal by denitrification in the reservoir were assumed to be the difference between N inputs to and outputs from the reservoir. The N inputs included N discharged from the three streams and atmospheric N deposition directly onto the reservoir surface. The three stream sampling sites closest to the reservoir were used to determine the average N concentrations in the stream discharge into the reservoir. As stream N concentrations were monitored at two-week intervals, we took this as the average concentration for the 2 weeks and then multiplied it by the calculated stream discharge

volume in this period to derive the stream N discharge into the reservoir. The N output is the N discharged from the reservoir gate which was determined by multiplying the recorded discharge flow and the corresponding N concentrations on each discharge day.

For the streams and ponds, it is difficult to monitor the N input and output and to differentiate between N storage and denitrification. We therefore used denitrification rates measured by the acetylene inhibition method as relative indicators of sediment storage and denitrification, with N storage and denitrification in the streams and ponds estimated from their denitrification rate relative to that of the reservoir and the N reduction in the reservoir measured by difference. For measurement of sediment denitrification with the acetylene method, intact sediment cores 0–50 mm deep from 12 sites in the reservoir, 10 sites in one of the streams and five ponds were sampled every 3 months from May 2007 to February 2008. Unfiltered water was taken simultaneously from the same locations as sediment samples for incubation at room temperature. The procedure followed that of Knowles (1990).

Nitrogen output through food/feed export and crop residue burning

To calculate field N output through food/feed export and crop residue burning, it is necessary to know the residue/yield ratios and N content in grains and crop residues. In 2007, above-ground samples of rice, maize, wheat, and oil rape were taken from ten farms to measure their residue/yield ratios and N contents in grains and crop residues. Nitrogen content in crops was measured by the Kjeldahl method. Residue/yield

ratios and residue N contents of soybean and cotton were taken from Deng et al. (2007).

Most crop residues in the watershed are burned in the field or for household energy with the other portion returned to the fields. During burning, a significant amount of the N contained in the crop residues is emitted to the atmosphere as NH_3 and NO_x (Andreae and Merlet 2001) and the rest is assumed to be emitted as N_2 . The fate of the crop residues was obtained through the household interviews, and N contents in the crop residues were either measured or obtained from the literature as described above. The parameters for the calculation are shown in Table 1.

Uncertainty analysis

To gain insight into the uncertainty in the N inputs and outputs, an uncertainty analysis was performed using Monte Carlo simulation. This method quantifies the uncertainty of each model parameter by characterizing its distribution function. In performing the Monte Carlo simulation, we assumed all the model parameters followed a normal distribution, with corresponding mean values and standard deviations. For activity data such as the application rates of N fertilizer, the amount of burned biomass, the means and standard deviations were based on survey. For parameters that were actually measured in the watershed such as NH_3 volatilization from applied fertilizer, riverine N discharge and sediment denitrification, the means and standard deviations were directly obtained from measurements. For other parameters such as NH_3 emission rates from animal excreta, the means were obtained from literatures as

Table 1 Parameters for the calculation of N output through food/feed export and crop residue burning^a

Crop	Yield (kg ha ⁻¹)	Residue/grain ratio	N content in grain (kg N kg ⁻¹)	N content in residue (kg N kg ⁻¹)	Burned percentage of residue
Rice	7,254	0.9	0.019	0.010	75
Wheat	4,770	1.1	0.028	0.0056	97
Maize	4,248	1.0	0.014	0.0059	88
Oil rape	2,452	2.2	0.034	0.0067	100
Soybean	1,779	1.0	0.051	0.021	100
Cotton	2,390	2.0	0.039	0.012	100

^a Data for crop yield and burned percentage of residue were obtained through household interviews. Residue/grain ratio, N content in the grain and residues for rice, maize, oil rape and wheat were measured, those for soybean and cotton were obtained from (Deng et al. 2007)

mentioned above. When the standard deviations of such parameters were not available from the literatures, coefficient of variation 20–30% was assumed. A total of 20,000 Monte Carlo simulations were performed. In each simulation, a set of model parameters was randomly generated according to their respective distribution function.

Results

Hydrology

Total precipitation from July 2007 to June 2008 (2007 water year) was 1,152 mm, and from July 2008 to June 2009 (2008 water year) was 1,014 mm. Rainfall occurred in each month, but heavy downpours usually occurred in July and August (Fig. 2). There was no external water source for the watershed. All stream discharge resulted from precipitation in the watershed. Significant stream discharge only occurred after heavy rainfall events. Total stream discharge into the reservoir was 14.6 and 7.8 million m^3 in the 2007 and 2008 water years, respectively, which translates to an average run-off of 361 mm in the 2007 water year and 189 mm in the 2008 water year for the area in the watershed excluding the reservoir.

Nitrogen concentrations in stream water and reservoir discharge

We show the average stream N concentrations of the 14 sites in Fig. 3. TN concentrations ranged from

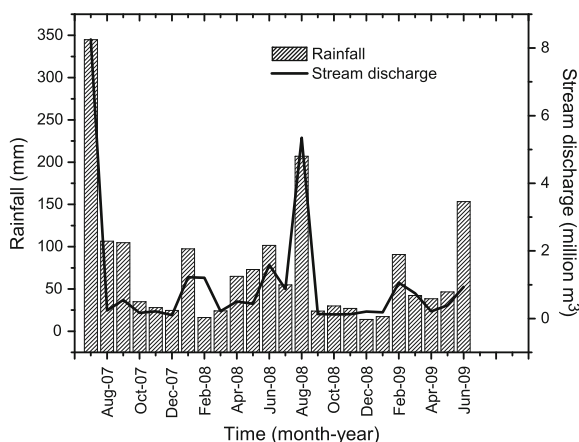


Fig. 2 Monthly rainfall and stream discharge of the watershed

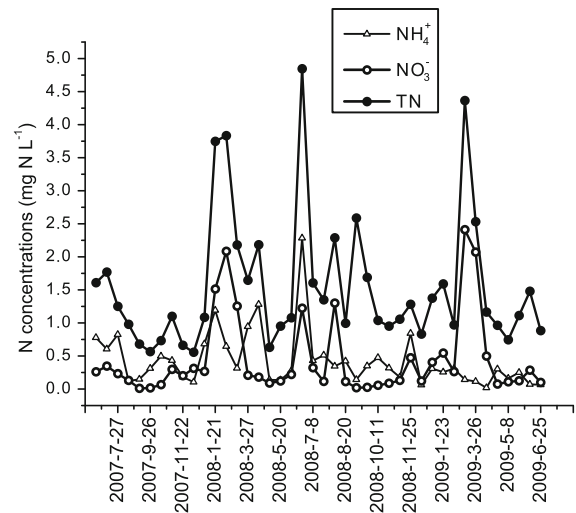


Fig. 3 The NH_4^+ , NO_3^- and TN concentrations in the stream water. The values were averaged for the 14 sites along the three streams in the watershed

0.5 to 4.8 mg N l^{-1} in the two water years. The arithmetic mean of the 42 measurement events on the 14 sites was 1.55 mg N l^{-1} . Peak concentrations happened in January, February and June of 2008 and March of 2009. The peak in February 2008 and March 2009 occurred after snow melt. The peak in June 2008 followed basal fertilization for rice and maize and a heavy rainfall on June 19. Nitrate concentrations ranged from below detection limits to 2.4 mg N l^{-1} , and averaged 0.45 mg N l^{-1} during the two year period. Peak concentrations of NO_3^- occurred simultaneously with TN. Ammonium concentrations were less variable as compared with NO_3^- and were consistently $<1.0 \text{ mg N l}^{-1}$ except on a few occasions.

The monthly average TN concentration in stream discharge generally showed a positive correlation with stream discharge volume (Fig. 4). Stream discharge was distinctively higher in the flooding season (8.2 million m^3 in July 2007 and 5.4 million m^3 in August 2008). Accordingly, the total N concentration was nearly 2 mg N l^{-1} in these periods. However, highest monthly average N concentrations were always in winter after snow melting (January and February 2008 and February and March 2009, symbols in the circle of Fig. 4).

The TN concentrations in the water sampled from the discharge gate of the reservoir were in most cases $<1 \text{ mg N l}^{-1}$ (Fig. 5), and the flow-weighted mean

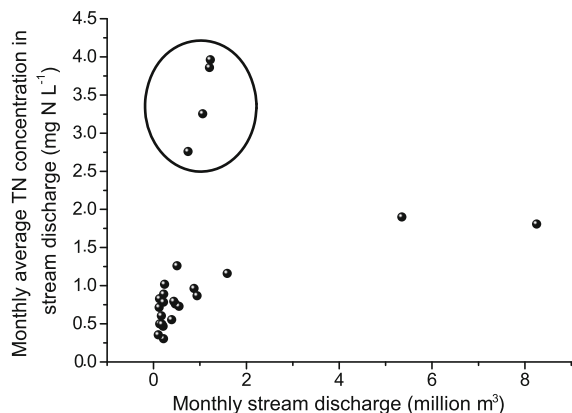


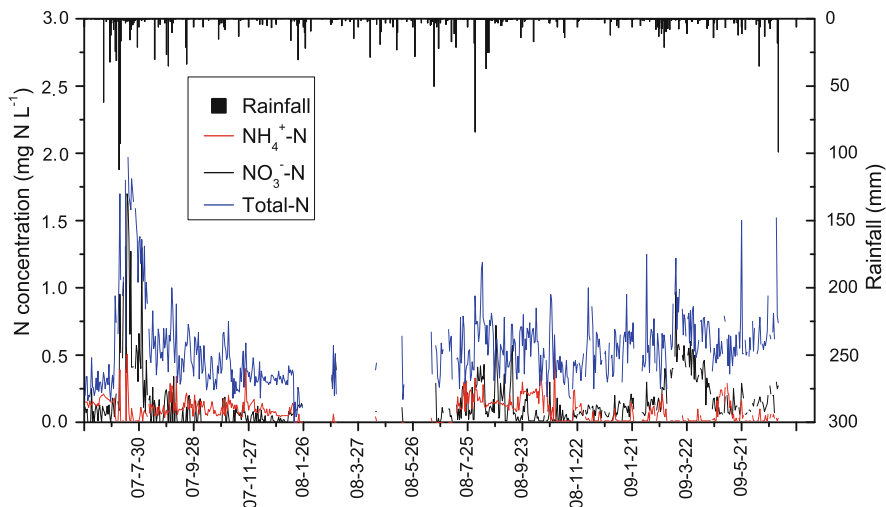
Fig. 4 Relationship between monthly stream discharge volume and average TN concentration in stream discharge. Symbols in the *circle* indicate data for January and February 2008 and February and March 2009

was 0.80 mg N l^{-1} in the two water years. TN with concentrations of $>1 \text{ mg N l}^{-1}$ lasted for about one month only after heavy rainfall on three consecutive days in early July 2007 (totaling 221 mm), and occasionally occurred in the remainder of the two years, mainly after heavy rainfall or snow melt. Flow-weighted mean concentrations of NO_3^- and NH_4^+ were 0.31 and 0.13 mg N l^{-1} , respectively.

N storage and/or removal in reservoir, streams and ponds

When compared on the same sampling days, TN, NO_3^- and NH_4^+ concentrations in the reservoir discharge were, in most cases, lower than those in the

Fig. 5 Nitrogen concentrations in the discharge water from the reservoir



stream discharge (Fig. 6), indicating N storage and/or removal by the reservoir. Average N input to the reservoir from stream discharge and atmospheric deposition was $28.1 \text{ Mg N year}^{-1}$, and total discharged N from the reservoir was $9.3 \text{ Mg N year}^{-1}$; therefore N storage and/or removal by the reservoir was estimated at $18.8 \text{ Mg N year}^{-1}$, or $75.4 \text{ kg N ha}^{-1}$ of water surface yr^{-1} .

Similar N processes should also happen in the streams and ponds. However, as the N source of the streams is areal, it is difficult to quantify N input. We used the sediment denitrification rate, measured by the acetylene inhibition method, as a surrogate to indicate the relative strength of N storage and/or removal, though denitrification rate measured by this method was much lower than that measured by mass balance method (Li et al. 2010). The results are shown in Fig. 7. On average, the denitrification rate of the stream and pond sediment was 175 and 110% of that of reservoir sediment, respectively. By considering the N storage and/or removal rate of the reservoir measured by the difference method, and the total area of the streams and ponds, we estimated the stream N storage and/or removal to be 3.9 Mg year^{-1} or 132 kg N ha^{-1} of water surface year^{-1} . Similarly, we estimated N storage and/or removal in ponds to be $11.6 \text{ Mg year}^{-1}$ or 83 kg N ha^{-1} of water surface year^{-1} .

Nitrogen budget and uncertainties

Although relevant monitoring was conducted for two consecutive years from July 2007 to June 2008, the

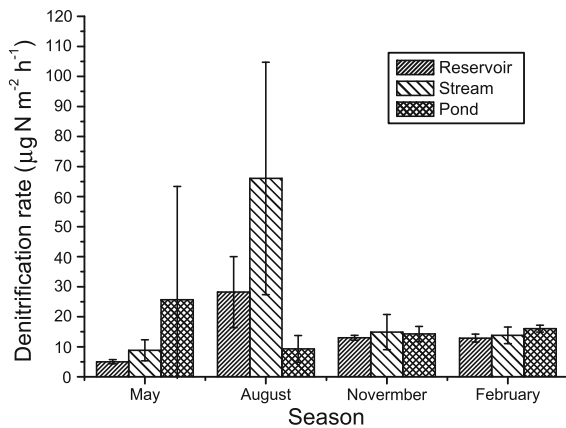


Fig. 6 Sediment denitrification rates of reservoir, stream, and pond measured by the acetylene inhibition method. Error bars indicate standard deviation of three replicates

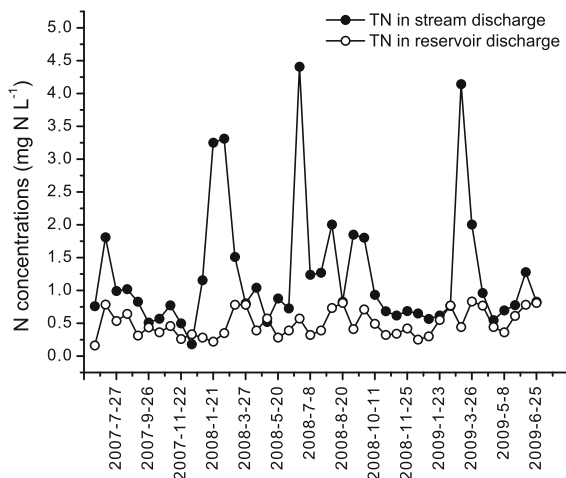


Fig. 7 Comparison of TN concentrations in the stream discharge and reservoir discharge on the same date. Total N in stream discharge was the arithmetic average of the three sites closest to the reservoir, each representing one stream

agricultural activity data obtained through the household interviews cannot be taken as being for a specific year because farmers reported what were their ‘general values’. We therefore calculated the N budget as for a ‘normal year’ (Fig. 8, Table 2). Chemical fertilizer was by far the dominant N input, totaling 1,001 Mg year⁻¹. Nitrogen fertilization rates were very heavy in the watershed. Average application rates for rice were 329 kg ha⁻¹, and for upland crops were 202 kg ha⁻¹. Because most of the arable lands were cropped twice a year, the annual N application rate was nearly 500 kg N ha⁻¹ of cropland.

However, our survey results showed there was large variability in N application rates among individual farmers. For example, the coefficient of variation (CV) of N application rate for rice was 32% and that for maize was 41%. Accordingly, Monte Carlo simulation showed that total fertilizer N input to the watershed ranged between 766 and 1,236 Mg N year⁻¹ (95% uncertainty range).

Total atmospheric N deposition to the watershed was 176 Mg year⁻¹, and biological N fixation was 87 Mg year⁻¹, accounting for 6.85% of the total N input. Nitrogen input through food/feed import was only minor, being 8 Mg year⁻¹, mainly in the form of crop seed. Due to the lack of measurement data, CVs of 20, 30, and 15% were assumed to account for the uncertainties in N deposition, N fixation and import, respectively. As a result, total N input from these three sources ranged between 191 and 351 Mg year⁻¹ (95% uncertainty range).

Food/feed export was the major N output, accounting for 41.5% of the total output. The simulated 95% uncertainty range for N output through food/feed export was 206–322 Mg year⁻¹. There was also a large N output through NH₃ emissions from chemical fertilizer and human/livestock waste. Field measurements showed that on average, 10% of the applied chemical fertilizer was volatilized as NH₃, with a higher rate for summer crops and lower rate for winter crops. The 95% uncertainty range for this N output was 73–134 Mg year⁻¹ as a result of the variability in N application rate and NH₃ volatilization ratio. 84 Mg N year⁻¹ was emitted from human/livestock waste as NH₃ during storage and after being applied to fields, with a 95% uncertainty range of 59–109 Mg year⁻¹. Most of the crop residues were burned, either in fields or in houses as biofuel, which resulted in N outputs of 140 Mg year⁻¹, in the form of N₂, NH₃ and NO_x emissions. Total aquatic storage/removal (in reservoir, streams and ponds) was estimated at 34.3 Mg year⁻¹, accounting for 2.7% of the total N input or 5.4% of total N output. Due to the large spatial and seasonal variability in measured denitrification rates, the 95% uncertainty range of aquatic N storage/removal was estimated to be 9.5–59.5 Mg year⁻¹. The average N output through discharge from the reservoir was only 9.3 Mg year⁻¹.

The unbalance N amounted to 637 Mg year⁻¹, with a 95% uncertainty range of 400–874 Mg year⁻¹. The estimated uncertainty arises from the variability in

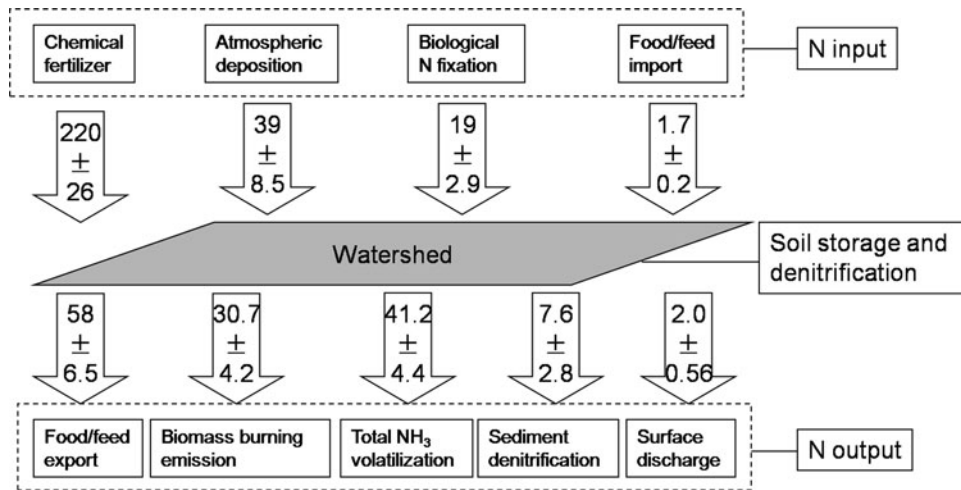


Fig. 8 Watershed N budget. Values are mean ± standard deviation, in kg N ha⁻¹ year⁻¹, and averaged for the total watershed area of 4,550 ha

Table 2 Nitrogen budget for Jurong Reservoir watershed, average for water year 2007–2008

Items of input and output	Mean (Mg N year ⁻¹)	95% uncertainty range (Mg N year ⁻¹)
Input		
Chemical fertilizer	1,001	757–1,236
Atmospheric deposition	176	101–251
Biological fixation	87	61–112
Food/feed import	8	6–10
Total	1,272	1024–1,520
Output		
Food/feed export	264	206–322
Fertilizer NH ₃ volatilization	104	73–134
Waste NH ₃ volatilization	84	59–109
Biomass burning emissions	140	103–177
Sediment storage/removal	34.3	9.5–59.5
Reservoir discharge	9.3	4.4–14.2
Total	632	540–715
Balance		
Input–output	637	400–874

activity data such as fertilization rate and in the N flux parameters such as the NH₃ volatilization ratio of the applied fertilizer. Top contributors to the uncertainty included fertilizer N application rate, N deposition rate, amount of food/feed export, and the aquatic storage/removal rate.

Discussion

Potential causes of low riverine N export

Nitrogen export by large rivers has been shown to account for 25% of the net anthropogenic N input (NANI) of their drainage basins (Howarth et al. 1996), and NANI has a good correlation with the proportion of agricultural land in the watersheds (Boyer et al. 2002). Our studied watershed is an intensive agricultural watershed, with an average N input of 280 kg N ha⁻¹ of watershed area year⁻¹. The total riverine N discharged from the reservoir was, however, 2.0 kg N ha⁻¹ year⁻¹, with a flow-weighted average concentration of 0.8 mg N l⁻¹. Without considering N removal by the reservoir sediment, total stream N discharge was 4.2 kg ha⁻¹ year⁻¹, accounting for 1.5% of the NANI, with a flow-weighted mean of 1.55 mg N l⁻¹. These values are low compared with other watersheds, especially those with a large percentage of agricultural land. For example, in a 101 km² watershed with 89% of its area being planted with maize and soybean in east-central Illinois, Gentry et al. (2009) found that the riverine discharge was 21–50 kg N ha⁻¹, or 13–32% of the NANI, with an average N concentration of 11–14 mg N l⁻¹. In a 19.4 km² watershed with 90% being agricultural land in Italy, Ventura et al. (2008) found that riverine N export was around 9.4 kg N ha⁻¹ and 5% of the NANI. Some watersheds in California have been

reported to have a small riverine N export rate of about 2 kg N ha^{-1} , but they contain a large proportion of natural land (Sobota et al. 2009).

We suggest that the low riverine N export in this study resulted from the characteristics of our rice paddy-dominated agricultural watershed. First, in a rice paddy-dominated watershed, rice paddies are usually found in lower parts of the landscape. The run-off generated from croplands in the upper parts can be intercepted by paddy fields below. Also, the many small ponds used to store irrigation water in such watersheds help to intercept run-off. There is a 12.5 km^2 residential and construction area in the watershed which mostly has water-impermeable ground. Precipitation of over $1,000 \text{ mm area}^{-1}$ on this residential area would produce run-off of at least 12.5 million m^3 . The measured average run-off from an upland field was 220 mm . If that is representative of all the uplands in the watershed, it would result in run-off of about 3 million m^3 from the uplands. There was also likely to be run-off from other land uses. However, the average stream discharge to the reservoir was $11.7 \text{ million m}^3 \text{ year}^{-1}$. Therefore, a significant proportion of the run-off generated from the various land uses would have been intercepted by the rice paddies and ponds in the watershed. As shown in Fig. 4, monthly stream N concentration shows a positive correlation with stream discharge volume, and, accordingly, stream N export is highly related to discharge volume. A similar phenomenon was reported by Howarth et al. (2006).

Second, unlike the pipe or tile-drained watersheds in the USA and Europe, there are no subsurface drainage facilities in the studied watershed, which is common for paddy-dominated watersheds in China and southeast Asian countries (e.g., Yoshikawa et al. 2008). Tile drainage greatly increases the transport efficiency of NANI to streams while poor surface and subsurface drainage enhances soil denitrification (McIsaac and Hu 2004). Another potential cause of the low riverine N export in the watershed was riparian denitrification, which can be an effective means for removing N in agricultural watersheds (Konohira et al. 2001). We have estimated the in-stream N removal to be $3.9 \text{ Mg N year}^{-1}$ in the watershed. Unfortunately, riparian denitrification was not measured due to difficulties with the methodology, but riparian zones did exist around the three streams in the watershed.

In summary, the characteristics of paddy-dominated watersheds greatly influence the hydrologic flow path, increase the water residence time and the transport of N and associated elements as compared to other watersheds.

In addition, the low proportion of riverine N export in this watershed is also due to the fact that N is subject to other losses and export. Most of the N inputs were on croplands through N fertilization and fixation, and this part of N inputs is susceptible to NH_3 volatilization and biomass burning, as well as food export. On average, 10% of the chemical N fertilizer was volatilized as NH_3 in the watershed, which is typical of the region (Tian et al. 2001, Ju et al. 2009). Most of the crop residues in the watershed were burned either in the fields or in houses as fuel, and N outputs through food export accounted for 21% of the NANI, which may not be the case in large scale watersheds.

Environmental implications of N export from rice paddy-dominated agricultural watersheds

Due to the above characteristics, the studied rice paddy-dominated agricultural watershed actually served as a purifier of atmospheric N because the stream discharge and reservoir discharge contained much lower N than the rain water. Flow-weighted TN concentrations in stream and reservoir discharges were 1.55 and 0.80 mg N l^{-1} , respectively, while that in the rain water was 2.94 mg N l^{-1} . This phenomenon has been reported for another rice paddy dominated watershed in Indonesia (Yoshikawa et al. 2008). Although there have been many watershed N budget studies, most of them listed only the amount of N inputs and outputs, and very few listed or allowed the calculation of N concentrations in rain water and river discharge. We compared the N concentrations in rain water and river discharge of our study and those that did list or allow the calculation of the N concentration in Fig. 9. It seems that only paddy-dominated agricultural watersheds and some watersheds with a high proportion of natural (unmanaged) land can remove N in rain water.

Plot scale field experiments on rice–wheat rotations often report run-off losses of 2–5% of the applied N (Zhu and Chen 2002). Stream N export was less than 1.5% of the total NANI in our watershed, lower than in the field experiments. This discrepancy

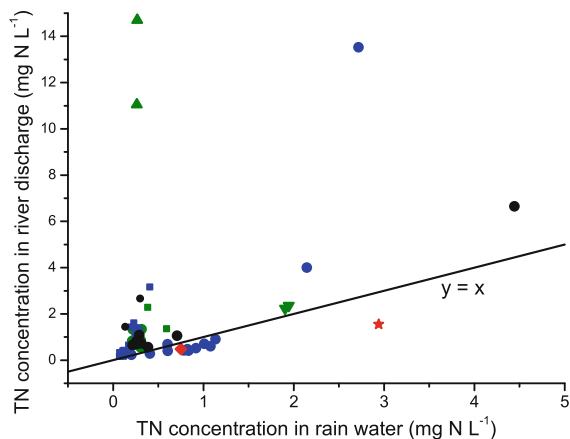


Fig. 9 Comparison of N concentrations in rain water and river discharge. *Green symbols* indicate watersheds with agricultural land use >25%, *red symbols* indicate rice paddy-dominated agricultural watersheds, *blue symbols* indicate watersheds with natural land use >80%, and *black symbols* indicate other watersheds. Data source: *filled triangle* (Gentry et al. 2009), *filled inverted triangle* (Ventura et al. 2008), *filled circle* (Schaefer and Alber 2007; Schaefer et al. 2009), *filled square* (Sobota et al. 2009), *filled diamond* (Yoshikawa et al. 2008), *filled star* (This study). (Color figure online)

was likely due to nitrogen storage and removal in the ponds, streams and riparian zone that could not be accounted for in plot scale field studies.

The NANI for the studied watershed was 280 kg ha^{-1} , while that for the whole of the Yangtze River region was about 76 kg N kg^{-1} (Xing and Zhu 2002), indicating that this is an intensive agricultural region. However, TN concentrations in the discharge water from the watershed, after N removal by the reservoir, were 0.8 mg N l^{-1} , much lower than that in the Yangtze River, which was about 1.4 mg N l^{-1} (Shen et al. 2003). The TN concentration at the mouth of the Qinhuai River, where the watershed is upstream, was more than 4 mg N l^{-1} (Environment Bulletin of Nanjing 2008, available at http://njrb.njnews.cn/page/61/2009-06/05/A7/20090605A7_pdf.pdf). All these data suggest that high fertilizer N input to rice-dominated agricultural watershed does not necessarily result in high N loading to streams and rivers that will exacerbate problems with eutrophication. The N concentrations in the discharge from the agricultural headstream are enhanced by other sources such as intensive husbandry, sewage sludge, and point sources when flowing downward through a more populous area. Although there is a population

density of nearly $400 \text{ people km}^{-2}$ in the studied watershed, human waste was not directly discharged to the waterways, but rather was stored for several months and then applied to fields as organic fertilizer. Therefore, it seems likely that in undeveloped areas, the impact of the human population on water quality will be limited, and in a well developed area where human waste is treated, the impact of human population will also be limited. However, in semi-developed areas such as the townships in eastern China, where human waste is flushed but not collected and treated, the population could greatly impact water quality.

It is worth noting that there was a large N output through atmospheric emission. Total N export through biomass burning emissions, NH_3 volatilization from chemical fertilizer and manure were $328 \text{ Mg N year}^{-1}$ in the watershed, of which 246 Mg was reactive N (NH_3 and NO_x). Given that there was a high atmospheric N deposition rate, the net reactive gaseous N output from the watershed was estimated at $70 \text{ Mg N year}^{-1}$, which was about eight times the output through riverine discharge and accounted for 5.5% of the NANI. Therefore, gaseous losses were by far the dominant processes that affected N cycling in such an agricultural watershed. In most watershed N budget studies, biomass burning emission of N was not accounted for (e.g., (Boyer et al. 2002; Schaefer et al. 2009; Sobota et al. 2009)). However, it was a significant N output in this studied watershed, accounting for 11% of the NANI. But this is not unusual. In another rice-dominated agricultural watershed in Indonesia, biomass burning emissions accounted for 37% of the total NANI (Yoshikawa et al. 2008).

Fate of surplus N

The unbalanced N amounted to 637 Mg year^{-1} in the watershed, or $155 \text{ kg N ha}^{-1} \text{ land year}^{-1}$. While this result might be partially due to uncertainties in the estimations of the inputs and other outputs, it is a huge amount of surplus N, accounting for 50% of the total input. The fate of this surplus N includes leaching to underground water, soil storage and denitrification. Leaching losses are difficult to quantify at a watershed scale, but field studies conducted in surrounding regions have shown that they were only 2–6% (mean 3%) of the applied chemical

fertilizer N (Zhu and Chen 2002). Fertilizer application rates have been heavy for the last two decades. Assuming that 20% of the unbalanced N was stored in the top 0.2 m of the soils during the last two decades, the soil N content in the watershed would have increased by 0.34 g kg^{-1} on average, and would be significantly more on croplands. However, the average soil N content of the uplands was 0.74 g kg^{-1} in the early 1980s (Zhang et al. 1986) and 0.75 g kg^{-1} in 2007 (measured data), and the soil N content of the paddy fields was $0.73\text{--}1.21 \text{ g kg}^{-1}$ in the early 1980s (Zhang et al. 1986) and $0.83\text{--}1.22 \text{ g kg}^{-1}$ in 2007 (measured data), showing no clear increase. The majority of the surplus N is therefore more likely to have been denitrified in the soils. Assuming 70% of the unbalanced N is denitrified in cropland soils, the average soil denitrification rate would be about 179 kg N ha^{-1} , which accounts for about 42% of the chemical N applied to croplands in the watershed. This estimated rate is close to rates measured in fields in this region using the ^{15}N tracing method. For example, Cai et al. (1992) found that 40.7–48.2% of the N applied to rice field was lost through denitrification. Similarly, on a field with a rice–wheat rotation in this region, Ju et al. (2009) showed that 36.4% of the 300 kg N ha^{-1} applied to rice and 43.5% of the 250 kg N ha^{-1} applied to wheat were lost through denitrification. While this high denitrification rate is desirable for the removal of excessive N, it may result in significant nitrous oxide (N_2O) emissions. Based on available multi-year data of N_2O emissions over the whole rice–wheat rotation cycle at 3 sites in southeast China, Zou et al. (2005) calculated that the fertilizer-induced N_2O emission factor was 1.02% for the rice season and 1.65% for the wheat season. Both are higher than the IPCC default emission factors (IPCC 2007).

Conclusions

Our monitoring and budget calculations demonstrate that, for rice paddy-dominated agricultural watersheds, although total N input is high, riverine N output can be $<1.5\%$ of the N input, as low as that in watersheds with a large proportion of natural land uses. This is because the watershed can intercept some of the run-off and greatly enhance soil denitrification. Monitoring showed that stream N

concentrations were lower than that in rain water, a phenomenon only found in rice paddy-dominated agricultural watersheds and natural watersheds. However, agricultural activities resulted in much more reactive N emission to the atmosphere than to the water. Net emission (emission minus deposition) of reactive gaseous N accounted for 5.5% of the total N input. Soil denitrification was estimated to be over 150 kg N ha^{-1} of land per year.

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