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RESEARCH ARTICLE

Utilizing water characteristics and sediment nitrogen isotopic features to identify non-point nitrogen pollution sources at watershed scale in Liaoning Province, China

Jian Ma · Xin Chen · Bin Huang · Yi Shi · Guangyu Chi · Caiyan Lu

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Abstract Identifying nitrogen (N) pollution sources is the fundamental work of non-point source pollution load reduction from watersheds, but is hard due to complex N transport and transformation within spatially heterogenized huge areas. During September 2011, we measured water characteristics and sediment N stable isotope in four tributaries of the upper reach of the Hun River, an important water source of the Dahuofang Reservoir, a large drinking water source in Northeast China. Results showed that spatial changes in SO_4^{2-} and Cl^- contents in the tributaries were consisted with the changes in density of the population living along the tributaries. Sediment $\delta^{15}N$ from all tributaries showed a downstream increasing trend in line with the land use change, which is characterized as more farmlands and more people around the outlet area of each tributary. Principal component analysis indicated the population density had a strong impact on N in these tributaries in the low-flow period. Tributaries and villages close to the Dahuofang Reservoir should be the major N load control objects in reduction of non-point source nitrogen load from the upper reach of the Hun River.

Keywords Non-point source (NPS) pollution · Nitrogen stable isotope · Sediment · Pollution sources identifying · Watershed · Hun River

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Introduction

Non-point source (NPS) pollution has become a serious problem in China (Ongley et al. 2010) and has been concerned for many watersheds in China and other parts of the world (Kendall et al. 2007, Ouyang et al. 2012, Xu et al. 2012). Nitrogen (N) as the main NPS pollutant is critical for quality of aquatic ecosystems, since excessive N could lead to undesirable consequences such as water eutrophication (Carey et al. 2013). In watersheds, N derives from multiple sources including soil erosion, storm runoff, agricultural chemicals, sewage, and manure (Howarth 2008). Human activities such as land use change, hydrological modifications, and agricultural management measures affect N transport and transformation (Liu et al. 2005, Shen et al. 2008). Due to the huge area, spatial heterogeneity, multiple sources, and complex terrains in a watershed, it is hard to determine the source, pathway, and spatial distribution of N losses (Zhang and Huang 2011). To keep the water quality of watersheds, reducing N load to rivers is the fundamental work of NPS pollution control.

In the aquatic environment, N substances mainly exist in dissolved forms (Jansson et al. 1994). The features of N pollution in river water change often especially when sewage is discharged or rainfall occurs due to intensified N transformation or transportation. Repeated determinations of concentrations of N substances alone can only provide information on their temporal change trends within aquatic systems (Yue et al. 2013). To reduce N load efficiently requires assessments of relative contributions from different sources (Carey et al. 2013). Analyzing the land use-water quality relationship and identifying specific N sources are both the key aspects of watershed water quality research (Carey et al. 2013).

Sedimentation, assimilation by plants and microorganisms, and denitrification are considered the basic mechanisms of N removal in aquatic ecosystems. During N biotransformation, biological discrimination between the two stable isotopes ^{14}N and ^{15}N leads to natural isotopic fractionation (Søvik and Mørkved 2008). For the case of wastewater denitrification, the lighter form of nitrogen (^{14}N) is removed at a higher rate than the heavier form (^{15}N), leading to an increasing ^{15}N value for the remaining product (Miller et al. 2010). The river sediment, which may be assumed as a micro-ecosystem, would assimilate N and dissimilatorily remove N through denitrification. Under this scenario, the ^{15}N value of sediment in the polluted area will be eventually higher than in the unpolluted area of a river, allowing N stable isotope ratios ($^{15}N/^{14}N$) as a reliable indicator of the N source. In watersheds, identifying the major N source through river monitoring is the customary way. Frequent monitoring is needed to conduct this work. Relatively inactive mobility of ^{15}N in sediment allows it as a good indicator for tracing the N source in rivers. Combined analysis of water characteristics and N isotopic composition of sediment can provide more detailed information regarding the sources and potential transformations of N load in watersheds.

The Dahuofang Reservoir, located in Liaoning Province, is one of the largest artificial lakes in Northeast China (Wang et al. 2011). It provides drinking water for a population of 23 million. However, since the 1990s, the quality of the water entering this reservoir degraded, mainly due to the increase of total nitrogen (TN) content (Baohua et al. 2007). Recently, regarding the level of TN, the quality of water flowing into the reservoir degrades gradually from grade 2 (TN <0.5 mg l^{-1}) to grade 3 (TN<1.0 mg l^{-1}) of the Environmental Quality Standards for Surface Water (GB3838-2002, China) (Wang et al. 2011, Wu et al. 2007). To stop this trend, identifying the main N pollution source to the Dahuofang Reservoir is the precondition for N pollution control. The Hun River contributes 52.7 % of the total water input to the reservoir. The upper reach of the Hun River is consequently important in identifying the N source to the reservoir. In this paper, four tributaries of the upper reach of the Hun River were sampled to examine the water characteristics, sediment total N and $\delta^{15}N$ values. We utilized these multiple parameters to identify the main sources of non-point N pollution to the river and examine the link between the N pollution source and human activities. The factors affecting the spatial distribution of the major NPS N were revealed.

Material and methods

Outline of the study area

The upstream area of the Hun River is situated in the northeast of the Dahuofang reservoir with a mountainous forest terrain and a drainage area nearly 2700 km^2. It is also the primary N pollution source to the Dahuofang Reservoir (Tang et al. 2012). The altitude of this area is high in the east and low in the west with an average elevation change from around 1100 to 300 m. Forests cover nearly 67 % of the river's drainage areas, and agricultural and residential areas are mostly limited to the areas close to streams (Fig. 1). The average annual precipitation of this area is 804 mm, mainly occurring in summer (from June to early August). The average annual temperature is about 6.6 °C. River flow changes in this area are in line with rainfall variation during the rainy season. Most tributaries in this area are shallow, with depths ranging from 0.3 to 1.2 m. This area is poorly developed with few heavy industries and sewage facilities for rural areas. Villages and small towns are the foremost inhabitation pattern for people living there. In 2011, the population living in this area is about 260 thousand. The study was conducted at four main tributaries (Dasuhe, Nankouqian, Beisanjia, and Nanzamu) of the upper reach of the Hun River (Fig. 1). The land use patterns of the surveyed tributaries are similar, with more forest coverage in the upper reaches and more farmlands and residential areas situating along the tributaries at the outlet area. The detail information of these tributaries was listed in Table 1.

Sampling and processing

Between September 3 and 7, 2011, we collected water and surface sediment samples at 17 sites from the source to outlet sites of the four tributaries (Fig. 1). A drifting park is located in the river valley down from the site HR5 to the mainstream of the Hun River. Owing to the banning of entering and the canyon topography, we did not get samples down from site HR5 to the mainstream of the Hun River. The water samples from each site were sampled and stored with polyethylene plastic bottles pre-rinsed with distilled water. Sediments from those sites were sampled and sealed in clean plastic bags.

All the water and sediment samples were kept below 4 °C and transported to the laboratory for further analysis. The water samples were stored separately for each analytical procedure: major ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, and SO_4^{2-}), inorganic N (NO_3^-, NO_2^-, and NH_4^+), and dissolved N (DN, including both organic and inorganic N in water soluble form). Water samples for the above analysis were filtered with millipore filters (0.45-μm pore size, MF-Millipore, USA) before analysis. Sediment samples were dried at 60 °C for 24 h and grinded through a sieve of 0.15 mm before analysis for N isotope and TN. Electric conductivity and pH of the water samples were measured by a EUTECH PH510 pH analyzer. We obtained the

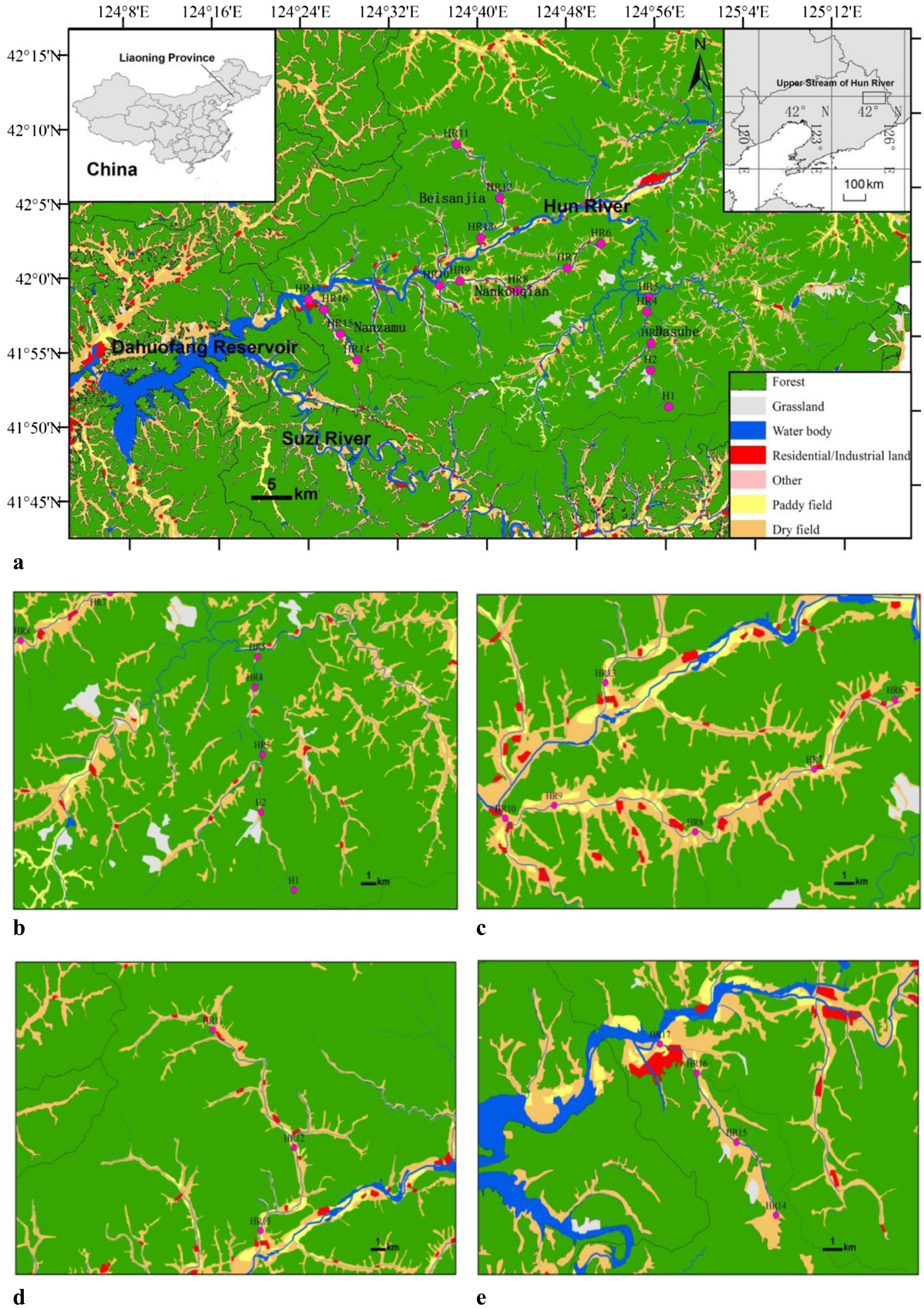

Fig. 1 Land use and sampling sites (*round points*) in the upper reach of the Hun River (**a**) with enlarged view of surveyed tributaries **b** Dasuhe, **c** Nankouqian, **d** Beisanja, and **e** Nanzamu

watershed area and social data (population, farmland, residential area, etc.) of each tributary, from the Statistics Bureau Ministry and Water Conservancy Bureau of Qingyuan County Government.

Table 1 Background information of the four surveyed tributaries

Tributaries	Drainage area (km^2)	Population (thousands)	Population density (people km^{-2})	Farmland area percent (%)	Villages/towns area percent (%)
Dasuhe	275	8.6	31	5.1	0.19
Nankouqian	334	23.4	70	16.3	0.61
Beisanja	273	14.7	54	2.6	0.46
Nanzamu	63.5	20.3	320	17.9	4.5

Laboratory analysis

Major ions in water samples were measured by ion chromatography DIONEX ICS-900. DN in water samples were analyzed by an analytikjena multi N/C® 3100 analyzer. TN in sediments were measured by hydrofluoric acid modification of the Kjedahl method (Bremner and Mulvaney 1982). For isotopic analysis, a Finnigan MAT DELTA plus XP stable isotope ratio mass spectrometer was used to analyze the TN isotope ratio ($^{15}N/^{14}N$), which was calculated by the standard equation: $\delta^{15}N=1000\times[(R_{sample}/R_{air})-1]$, where R_{sample} and R_{air} are the $^{15}N/^{14}N$ ratios for the sample and the atmospheric N_2 (international standard), respectively. The results were in units of parts per mil (‰), with standard errors better than ±0.15‰ for $\delta^{15}N$.

Data analysis

The differences in each specific ion content in water between sampled tributaries were tested by one-way analysis of variance (ANOVA) with a multiple comparison test (α=0.05). The least significant difference (LSD) test was used to assess the differences when the differences were found to be significant ($p\leq0.05$). Social data were used to examine the relationships of water characteristics and sediment $\delta^{15}N$ values with social variables. Principal component analysis (PCA) was used to reduce the number of variables. All statistical analyses were performed on IBM SPSS Statistic version 21.0.

Results and discussion

River water ions characteristics

The ion features of river water samples (Table 2) were similar as previously reported (Zhang et al. 2012), with SO_4^{2-}, NO_3^-, Cl^-, Ca^{2+}, and Na^+ being the dominant ions. This is consistent with the hydrological feature of this region that rainfall and forest runoff are the main sources of water in the upper reach of the Hun River. The Nanzamu tributary had significantly higher contents of SO_4^{2-} and Cl^- than the other tributaries, with average differences of 42.8 and 7.9 mg l^{-1} for SO_4^{2-} and Cl^-, respectively (ANOVA, $p\ll0.001$). This is consisted with the highest population density (320 people km^{-2}) from the Nanzamu tributary. Chemical fertilizers and detergents are an anthropogenic source of SO_4^{2-} in the water (Hosono et al. 2011), and sewage is an important source of Cl^- (Altman and Parizek 1995). Lower values for these two ions from the more eastern tributaries (Table 2) were consisted with their lower population densities (Table 1).

Spatial patterns of NH_4^+, NO_3^-, and DN in water

For the spatial distribution of NH_4^+, NO_3^-, and DN, there were no significant differences between the four surveyed tributaries according to ANOVA. Source samples from the Nankouqian tributary had the highest DN value compared to the source samples from the other three tributaries, mainly due to the presence of farmlands around its source site. A previous study around this area has confirmed that farmland non-point pollutants deteriorated the surface water quality during the low-flow period (Wang et al. 2013).

Nitrate N accounted for the highest ratio of DN in the tributary water samples, ranging from 66 to 99 %. Sharp increases in levels of N substances occurred in the Dasuhe and Nanzamu tributaries before they merged the main river. N fertilizers are often applied at rates over 400 kg N ha^{-1} in Northeast China (Ju et al. 2007). More field runoff and sewage drainage around the outlet areas of the two tributaries would cause higher N inputs into the tributaries. A downstream decline trend in levels of N substances in the Nankouqian and Beisanjia tributaries (Table 2, Fig. 1) was mainly ascribed to the effect of water dilution and mixing. Shallow sediment layer over the steep riverbed and fast water flows resulted in little presence of aquatic plants for N immobilization and aerobic condition (6.3–13.8 mg l^{-1} O_2 from the source site to the outlet) to greatly limit N removal through denitrification in the tributaries, while the low levels of NO_2^- detected at the source sites of Nanzamu tributary may come from the process of nitrification.

Chloride ion is conservative in natural water, and small changes in level of Cl^- were observed in the water flow (Table 2). The comparison between NO_3^- and Cl^- can be used to determine whether NO_3^- is conservative relative to Cl^- (Altman and Parizek 1995). Fertilizers and sewage are the source of both N and $C1^-$ (Altman and Parizek 1995). More fields and villages at the outlet areas of the tributaries were the common land use distribution patterns in this region (Fig. 1).

Table 2 Chemical analysis of water and sediment samples at various sites from four main tributaries of the upper reach of the Hun River

Tributaries	Site	Longtitude (°)	Latitude (°)	Altitude (m)	pH	Conductivity (μS cm^{-1})	Na^+ (mg l^{-1})	K^+ (mg l^{-1})	Mg^{2+} (mg l^{-1})	Ca^{2+} (mg l^{-1})	F^- (mg l^{-1})	Cl^- (mg l^{-1})	PO_4^{3-} (mg l^{-1})	SO_4^{2-} (mg l^{-1})	NH_4^+ (mg l^{-1})	NO_2^- (mg l^{-1})	NO_3^- (mg l^{-1})	DN (mg l^{-1})	Sediments Ave. (±SE) *n*TN (%)	Sediments Ave. (±SE) $\delta^{15}N$ (‰)
Dasuhe	HR1	124.93667	41.85139547		7.532		2.5	1.3	2.3	11.3	n.d.	1.7	u.d.	25.1	u.d.	n.d.	8.1	1.9	30.24 (0.1)	2.2 (0.2)
	HR2	124.91778	41.91003471		6.7108		3.9	1.3	3.3	17.6	0.1	3.0	u.d.	19.5	u.d.	n.d.	4.6	1.3	40.31 (0.1)	3.6 (0.6)
	HR3	124.90861	41.91083429		7.2142		4.2	1.7	3.2	17.7	0.1	3.1	u.d.	24.9	u.d.	n.d.	7.5	1.8	30.23 (0.02)	4.0 (0.2)
	HR4	124.90917	41.93639407		6.9127		3.4	0.7	1.9	9.5	n.d.	3.3	u.d..	11.9	u.d.	n.d.	21.2	5.5	20.14 (0.06)	3.3 (0.1)
	HR5	124.9175	41.96806369		8	154	2.1	1.2	1.4	6.9	n.d.	1.2	u.d.	5.9	0.1	n.d.	3.0	0.7	1 0.14	4.2
Nankouqian	HR6	124.83806	42.02694530		7.255		5.7	2.4	3.5	19.0	n.d.	3.5	u.d.	31.2	n.d.	n.d.	25.1	7.2	30.17 (0.2)	2.2 (0.1)
	HR7	124.80083	41.00139492		7.7160		5.7	3.3	3.7	16.7	0.1	3.3	u.d.	22.4	u.d.	n.d.	10.2	2.5	30.11 (0.1)	3.5 (0.1)
	HR8	124.72167	41.97583462		6.9121		4.7	1.5	2.9	15.5	0.1	1.5	u.d.	21.4	u.d.	n.d.	8.1	2.1	30.07 (0.02)	4.5 (0.1)
	HR9	124.60167	41.98556446		6.9117		6.4	2.8	4.6	22.4	0.1	3.2	u.d.	22.8	u.d.	u.d.	8.3	2.0	30.09 (0.02)	5.4 (0.1)
	HR10	124.55361	41.98861428		6.879		2.3	1.2	1.4	7.6	n.d.	1.1	u.d.	5.9	0.1	n.d.	1.6	0.4	40.21 (0.03)	5.9 (0.2)
Beisanjia	HR11	124.64694	41.13556496		6.357		3.9	1.7	2.7	12.7	n.d.	1.7	0.7	11.5	0.2	n.d.	5.4	1.8	30.17 (0.03)	3.7 (0.07)
	HR12	124.06972	42.09306477		7.3122		5.8	3.6	3.4	17.9	n.d.	2.6	u.d.	17.9	0.2	n.d.	5.3	1.6	20.04 (0.03)	5.2 (0.1)
	HR13	124.66611	42.03861469		7.387		2.6	1.7	1.6	8.8	n.d.	1.5	0.5	7.4	0.1	u.d.	2.0	0.6	30.12 (0.03)	5.8 (0.4)
Nanzamu	HR14	124.48002	41.89972232		7.1165		0.4	0.2	0.4	1.7	0.1	12.2	0.7	76.0	u.d.	0.4	13.2	3.2	20.45 (0.1)	2.6 (0.1)
	HR15	124.4525	41.93361214		7.4299		10.3	4.9	7.4	26	0.1	6.0	1.1	43.1	0.2	0.3	9.1	2.3	30.63 (0.2)	4.2 (0.1)
	HR16	124.43722	41.95028190		7.2320		10.1	2.7	6.5	28.9	0.1	9.7	u.d.	49.5	u.d.	n.d.	34.9	7.9	30.57 (0.08)	5.9 (0.1)
	HR17	124.40417	41.97472154		7.3303		11.2	2.3	9.4	32.8	0.1	11.5	u.d..	51.8	u.d.	n.d.	20.5	4.8	40.34 (0.1)	9.1 (0.7)

n.d. not detected, *u.d.* non-detectable

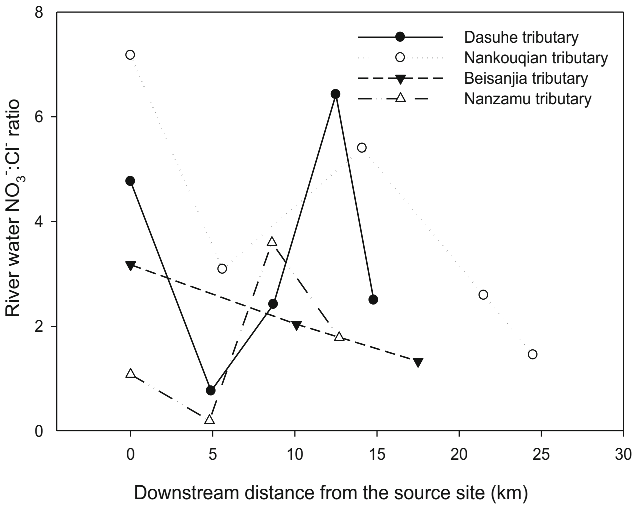

Fig. 2 Downstream changes in ratio of NO_3^- to Cl^- in the four tributaries

Compared to the relatively high ratio of NO_3^- to Cl^- at the source site, more field runoff and village sewage likely caused a much higher input of Cl^- relative to NO_3^-, resulting in the obviously lowered ratio of NO_3^- to Cl^- at the outlet site of each tributary (Fig. 2). In addition, N removal through denitrification in the sewage could not be fully excluded before being fully mixed with well-aerated water from the source site, also possibly lowering the ratio of NO_3^- to Cl^- in the tributary. More information beyond the measurement of the characteristics of river water, such as the measurement of the characteristic of sewage and farmland runoff, is needed to further reveal the changes in ratio of NO_3^- to Cl^- to the tributaries.

Identifying main N source based on sediment $\delta^{15}N$

The sediment $\delta^{15}N$ values showed a similar downstream trend of increase for each tributary (Table 2, Fig. 3). Sediment N in the tributaries derived from various sources, including forest runoff, chemical fertilizers, sewage, and manure, each with a specific range for $\delta^{15}N$ value to affect sediment $\delta^{15}N$ value. The $\delta^{15}N$ values were typically around +0‰ for chemical N fertilizer, +2 to +5‰ for soil, and +8.0 to +20.0‰ for sewage and manure (Kendall and MacDonnell 1998, Liu et al. 2006, Kendall et al. 2007, Xue et al. 2009). In this study, the distribution of the sites with $\delta^{15}N$ values less than +5‰ suggested that N from forest and field soil runoff is the major nitrogen load at the source and upstream sites of each tributary (Table 2, Fig. 3).

$\delta^{15}N$ is very sensitive to reflect the input of anthropogenic N (Bowen et al. 2007) and the enrichment of $\delta^{15}N$ value by anthropogenic discharge can far exceed any differences caused by other processes, such as trophic enrichment (Miller et al. 2010). The downstream increasing trend of $\delta^{15}N$ values for each tributary suggested anthropogenic contributions primarily from village sewage and manure. Except for the Dasuhe tributary, the $\delta^{15}N$ values higher than +5‰ suggested that sewage and manure were both very important N sources to the downstream areas of the more western tributaries. Farmland is usually considered as an important pollution source to degrade water quality (Iscen et al. 2008). A previous study around this area indicated that NPS pollutants from farmland are the major threat to water quality of the Hun River (Wang et al. 2013). However, farmland runoffs depend more on rainfall events while N loads from villages are much more consistent and depend on human activities. Our results were obtained during periods with no significant rainfall events. The sediment $\delta^{15}N$ values suggested the contribution of N loads from villages to the tributaries was very important during such periods. Specifically, the relationship between sediment $\delta^{15}N$ values versus TN values in the Nanzamu tributary was found to be quite different from that in the other three more eastern tributaries, primarily due to the significant

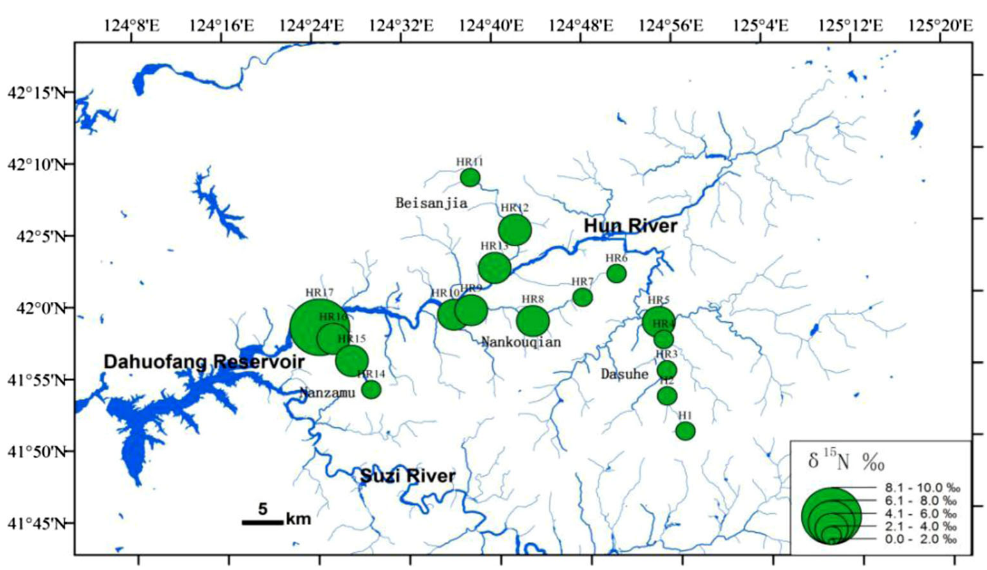

Fig. 3 Spatial changes in $\delta^{15}N$ value of sediment in the four tributaries of the upper reach of the Hun River

differences in TN value ($p<0.05$) (Fig. 4). It suggested the N sources for the four sampled tributaries were generally the same, but the Nanzamu tributary received more N load.

Anthropogenic nitrogen contributions

Together with results on sediment $\delta^{15}N$ values (Table 2) and their westward increase trend (Fig. 3), the positive relationships between the sediment $\delta^{15}N$ values at the outlet sites of each tributary and the population densities and the relative area ratios of villages of each sub-watershed (Fig. 5) suggested anthropogenic N from sewage and manure is the main NPS N source for the more western tributaries. PCA analysis between DN, $\delta^{15}N$, and the social variables (population, population density, and villages percent) (Table 3) showed that two principal components PC1 and PC2 respectively explained 73.4 and 23.5 % of the total variance, and loadings in PC1 were characterized as $\delta^{15}N$ (0.89), population density (0.99), and villages percent (0.98) (Table 3), further suggesting that the population density and village percent are important social variables for $\delta^{15}N$ values in the surveyed tributaries.

A positive trend of outlet $\delta^{15}N$ values of sediments with the population size of a watershed has been reported (Costanzo et al. 2005, MacAvoy et al. 2009, Miller et al. 2008, Miller et al. 2010), but was not observed in this study, likely due to the specific population distribution pattern along the four tributaries, where people mainly inhabit along the tributaries, especially at the outlet areas. A higher population density at a particular location of a tributary would cause more anthropogenic N load into the tributary.

Changes in $\delta^{15}N$ value as a time-averaged measure of past activities (Tieszen et al. 1983) are affected by a number of factors. In this study, rainfall events in the rainy season (June to August) would be one of the critical factors affecting N transportation and transformation in sediments of the four tributaries, due to steep riverbeds, fast water flows, and shallow sediment depths. Sediment $\delta^{15}N$ values likely vary to some extent during the rainy season but would much less in

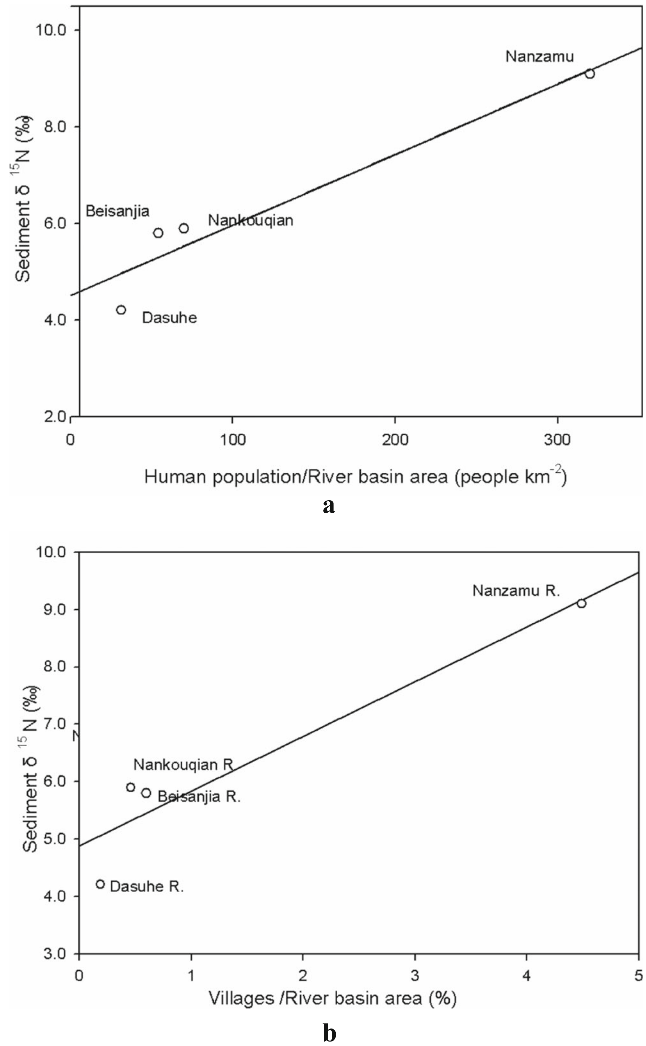

Fig. 5 Plot of sediment nitrogen stable isotope ratios at each tributary outlet site against the population density (number of people per square kilometer) (**a**) and the percent of villages (rate of villages to the whole sub-watershed area) (**b**) for each tributary. Regression of sediment $\delta^{15}N$ (R^2=0.92, 0.95, respectively) was significant (p=0.05)

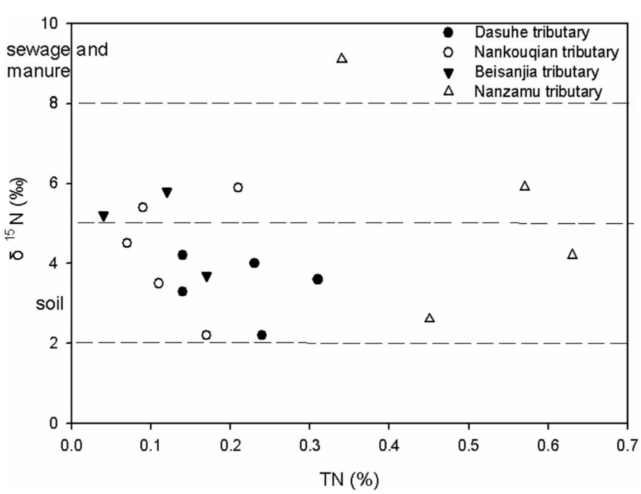

Fig. 4 Sediment $\delta^{15}N$ versus TN concentration of the four surveyed tributaries

Table 3 Component Matrix of DN and $\delta^{15}N$ to social variables performed by PCA

Component matrix[a]	Component	
	1	2
DN	0.77	−0.61
$\delta^{15}N$	0.89	0.35
Village percent	0.98	−0.18
Population	0.56	0.79
Population density	0.99	−0.11

[a] Two components extracted

the low-flow period if without anthropogenic impacts. Our survey was conducted in September, and the impact of rainfall would be small on the $\delta^{15}N$ values of the sediments. The observed spatial changes in $\delta^{15}N$ value of the sediment could be used as a reference to well reflect the anthropogenic contributions of N substances in the upper reach of the Hun River.

Conclusion

Spatial changes in river water characteristics such as contents of SO_4^{2-} and Cl^- and the ratio of NO_3^- to Cl^- and in sediment N isotopic values could be used together to provide more information for identifying the N load sources in the forest-dominated upper reach of the Hun River. Due to a relatively low ratio to the watershed area, farmlands are not the principal N source of the four sampled tributaries. Within each tributary, N load in the upstream area is primarily from forest runoff while N load in the outlet area may mainly derived from anthropogenic inputs with the greatest contribution from sewage and manure, especially in the low-flow period. With more people living close to the tributaries, especially around the outlet areas, the population density rather than the population size had a stronger impact on the NPS N load to the upper reach of the Hun River. Considering the capacity of river self purification and the spatial distribution of N in the upper reach of the Hun River, tributaries and villages close to the Dahuofang Reservoir should be the major N load control objects.

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