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Effects of land-use patterns on in-stream nitrogen in a highly-polluted river basin in Northeast China

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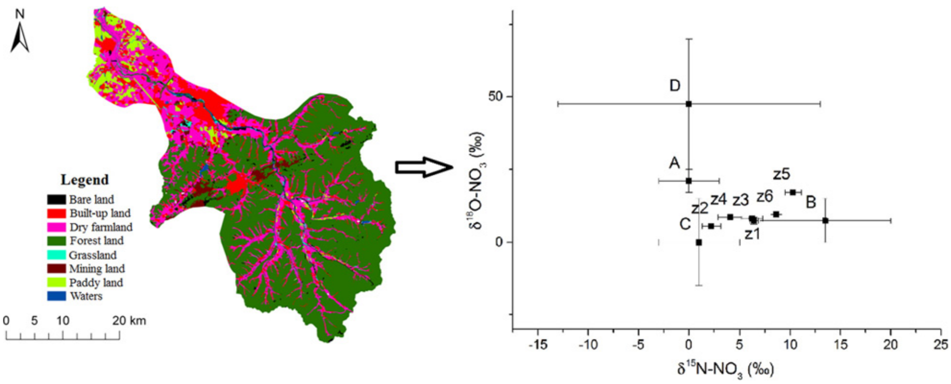
HIGHLIGHTS

- Land-use types were correlated well with most nitrogen variables over seasons.
- Built-up land dominated in predicting nitrogen variables during different seasons.
- Shape metrics predicted most nitrogen variables in different seasons.
- Nitrogen sources and their contributions were estimated using nitrate isotopes.
- Domestic sewage mainly contributed to river nitrogen pollution in residence zone.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigated the effects of land-use patterns on nitrogen pollution in the Haicheng River basin in Northeast China during 2010 by conducting statistical and spatial analyses and by analyzing the isotopic composition of nitrate. Correlation and stepwise regressions indicated that land-use types and landscape metrics were correlated well with most river nitrogen variables and significantly predicted them during different sampling seasons. Built-up land use and shape metrics dominated in predicting nitrogen variables over seasons. According to the isotopic compositions of river nitrate in different zones, the nitrogen sources of the river principally originated from synthetic fertilizer, domestic sewage/manure, soil organic matter, and atmospheric deposition. Isotope mixing models indicated that source contributions of river nitrogen significantly varied from forested headwaters to densely populated towns of the river basin. Domestic sewage/manure was a major contributor to river nitrogen with the proportions of 76.4 ± 6.0% and 62.8 ± 2.1% in residence and farmland-residence zones, respectively. This research suggested that regulating built-up land uses and reducing discharges of domestic sewage and industrial wastewater would be effective methods for river nitrogen control.

1. Introduction

Changes in land-use patterns have dramatically affected the river water quality by altering the natural appearance, material circulation, and energy distribution of landscapes within watershed ecosystems

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(Lee et al., 2009; Tran et al., 2010; Rothwell et al., 2010; Bu et al., 2014; Wilson, 2015). In-stream nitrogen pollution is due to alterations of runoff, non-point source pollution production, and nutrient transportation driven by land-use changes (Mattikalli and Richards, 1996; Wilson, 2015). Generally, crop land within a watershed has a strong influence on nitrogen loadings in river water due to the utilization of nitrogen fertilizers (Ngoye and Machiwa, 2004; Woli et al., 2004; Wang et al., 2014). Expansion of built-up land including industrial and urban land uses also results in increased nitrogen in river water due to the nitrogenous wastewater discharges (Schoonover and Lockaby, 2006; Wilson, 2015). Forest lands can provide mitigating and removing effects on riverine nitrogen due to their fixation and absorption effects for nutrients (Nakagawa and Iwatsubo, 2000; Piatek et al., 2009; Bu et al., 2014). Consequently, land-use patterns to some degree determine in-stream nitrogen concentrations.

The pollution sources of river nitrogen can be identified by the dual isotopic composition of nitrate ($\delta^{15}N–NO_3$ and $\delta^{18}O–NO_3$). The isotopic compositions of atmospheric nitrogen deposition range from −13‰ to +13‰ for $\delta^{15}N–NO_3$ (Lee et al., 2008; Xue et al., 2009) and from 25‰ to 70‰ for $\delta^{18}O–NO_3$ (Kendall et al., 2007). Nitrate originating from manure or sewage is usually characterized by $\delta^{15}N–NO_3$ values between +7‰ and +20‰ or more (Mayer et al., 2002) and $\delta^{18}O–NO_3$ values between 0‰ to 15‰ (Kendall et al., 2007), which is isotopically distinct from nitrate in synthetic fertilizers (−3‰ to +3‰ $\delta^{15}N–NO_3$ and 17‰ to 25‰ $\delta^{18}O–NO_3$) and natural soil organic matter (−3‰ to +5‰ $\delta^{15}N–NO_3$ and −15‰ to 15‰ $\delta^{18}O–NO_3$) (Kendall et al., 2007; Lee et al., 2008). The possible sources of nitrogen in rivers thus include synthetic fertilizer, domestic sewage/manure, soil organic matter, and atmospheric deposition.

The main factor influencing the nitrogen runoff in watersheds is landscape structure, especially land-use composition and its spatial configuration (Uuemaa et al., 2005). Land-use composition not only affects the watershed hydrological system but also closely relates to nitrogen inputs (Wang et al., 2014). The land-use spatial configuration is the most direct landscape characteristic influencing hydrological processes and nutrient cycles within watersheds (Turner et al., 2001; Woli et al., 2004; Bu et al., 2014). Landscape metrics that reflect the structural composition and spatial configuration of landscape patterns are directly or indirectly correlated with river nitrogen levels (Lee et al., 2009; Tran et al., 2010; Rothwell et al., 2010). Consequently, spatial analysis metrics and methods are suitable for quantifying the relationship between landscape patterns and nitrogen concentrations in watersheds.

Because river nitrogen pollution is induced by the changes of land-use patterns (Mattikalli and Richards, 1996; Uuemaa et al., 2005; Lee et al., 2009; Bu et al., 2014; Wilson, 2015), most studies have focused on the relationships between land use and riverine nitrogen (Bahar et al., 2008; Wang et al., 2014). Researchers seldom use isotope mixing models to link nitrogen sources and loadings from land use types and structure in watersheds. This study applies land-use analysis with geographical information systems in combination with natural-abundance isotope values of nitrate and source mixing models to evaluate the effects of land-use patterns on riverine nitrogen and calculate the contributions of different nitrogen sources in the Haicheng River basin in Northeast China. The Haicheng River is suffering serious nitrogen pollution and is contributing to the eutrophication of coastal ecosystems; its total nitrogen (TN) and nitrate nitrogen ($NO_3–N$) concentrations have reached to high levels (Bu et al., 2011). However, the influence of land-use patterns on river nitrogen is unknown in rivers with such high nitrogen pollution. Thus, the objectives of the current study are to: (1) investigate the effects of land-use types on river nitrogen pollution, (2) evaluate the effects of landscape pattern metrics on river nitrogen pollution, and (3) identify the principal sources of nitrogen pollution and calculate their contributions to river nitrogen using stable nitrate isotopes.

2. Materials and methods

2.1. Study area

The Haicheng River (40.48°–41.01° N, 122.48°–123.14° E) is a branch of the Taizi River in Northeast China. The river watershed covers an area of 1249.3 km^2 and drains a total length of 87.5 km in Haicheng City of Liaoning Province, Northeast China (Fig. 1a). It discharges an average of 2.17 m^3/s monitored at Longquan gaging station (Fig. 1a). The Haicheng River originates from Mt. Xiongdi in the southeast of Gushan Town, and then flows through Ximu Town, Haicheng City, Dongsi Town, Zhongxiao Town, and Niuzhuang Town in the direction of river flow. Finally, the river discharges into the Bohai Sea at Liaodong Bay after a confluence with the Taizi River (Fig. 1a).

The river basin is situated in a warm temperate monsoon climate zone and has four distinct seasons and abundant rainfall. The annual temperature in the basin ranges from −21.1 °C (in winter) to 35.9 °C (in summer) with an average of 10.4 °C. The annual average rainfall is 701.7 mm, and most rainfall occurs in summer (from June to August). The river flow co-varies with the rainfall because of the seasonality of the river, and has a peak discharge in summer season. The main soil types of the river basin include chromic cambisol, haplic phaeozem, cumulic hapludoll, and udic haplustalf (FAO, 2006). The vegetation coverage comprises 52.9% of the whole basin (Fig. 1b), including 3.6% of some orchards and managed forests for timber and firewood. Agricultural land covers 34.3% in the river basin, whereas built-up land is intensive in the middle and lower reaches of the river, covering 10.3% of the total area. The main farm crops along the river are maize and rice during the crop growing seasons from spring to autumn. The population in the river basin comprises 489,000 people (2010), most of whom live in rural areas (LHSB, 2011). Industries in the river basin principally include mining, mineral processing, textile printing and dyeing, and paper industries.

2.2. Water sampling and analytical methods

Four water sampling surveys were conducted in April, June, August, and October of 2010. The first sampling survey was set in spring before crop planting and fertilizer applications to local fields. The second sampling survey was in early summer, generally after cultivation and during fertilizer application. The third and fourth sampling surveys were conducted in late summer during significant runoff events and in fall after crop harvest. In each survey, thirty sampling sites (sites 1–30) were selected from the Haicheng River and its tributaries (Fig. 1a). The sampling strategy for the water sampling sites has been described previously (Bu et al., 2011).

River water was sampled in polyethylene plastic bottles which were prerinsed thrice with distilled water and then stored below 4 °C for the laboratory analysis of ammoniacal nitrogen ($NH_3–N$), $NO_3–N$, nitrite nitrogen ($NO_2–N$), and TN. Water samples for $NH_3–N$, $NO_3–N$, and $NO_2–N$ analyses were filtered with 0.45 μm pore size and 47 mm diameter membrane filters (MF-Millipore, USA) in the field. For measuring all nitrogen variables, water samples were also acidified to $pH < 2$ by sulfuric acid in situ and then were stored in polyethylene bottles for laboratory analyses.

Analyses were all conducted according to the national standard methods (NEPB, 2002). In the laboratory analyses, $NH_3–N$ and $NO_2–N$ were respectively determined by using Nessler's reagent and *N*-(1-naphthyl) ethylenediamine dihydrochloride spectrophotometry methods. $NO_3–N$ and TN were all quantified by alkaline potassium persulfate oxidation–UV spectrophotometry method. Detection limits of $NH_3–N$, $NO_3–N$, $NO_2–N$, and TN were 0.025, 0.02, 0.003, and 0.05 mg/L, respectively.

Water samples for measuring stable isotope compositions of $N–NO_3$ and $O–NO_3$ were prepared through anion exchange resins following the procedures described by Silva et al. (2000). The samples were eluted and then purified to produce silver nitrate (Pardo et al., 2004). The