Journal of Hydrology 545 (2017) 355–366

Contents lists available at ScienceDirect

Journal of Hydrology

journal homepage: www.elsevier.com/locate/jhydrol

Research papers

Hydrological and environmental controls of the stream nitrate concentration and flux in a small agricultural watershed

Y. Zhou [a], J.F. Xu [b], W. Yin [b], L. Ai [a], N.F. Fang [c], W.F. Tan [a], F.L. Yan [b], Z.H. Shi [a,c,*]

[a] College of Resources and Environment, Huazhong Agricultural University, Wuhan 430070, China
[b] The Yangtze River Water Resources Protection Science Institute, Wuhan 430051, China
[c] State Key Laboratory of Soil Erosion and Dryland Farming on the Loess Plateau, Institute of Soil and Water Conservation, Chinese Academy of Sciences, Yangling, Shaanxi 712100, China

ARTICLE INFO

Article history:
Received 9 October 2016
Received in revised form 6 December 2016
Accepted 8 December 2016
Available online 16 December 2016
This manuscript was handled by G. Syme, Editor-in-Chief

Keywords:
Nitrate
Watershed hydrology
Land use
Physiographic indices
Partial least squares regression

ABSTRACT

Nitrate exports from diffuse sources constitute a major cause of eutrophication and episodic acidification in inland aquatic systems, and remedial action requires the identification of the influencing factors associated with these nitrate exports. This paper examines the combined effects of watershed complexity on nitrate concentration and flux in terms of the hydrological and environmental factors in heterogeneous nested subwatersheds in the Danjiangkou Reservoir Area (DRA), China. We established 15 sampling sites in the main stream and tributaries and conducted biweekly sampling in 2008–2012 to monitor the nitrate exports. The hydrological and environmental indices within the watershed were divided into subwatersheds and considered as potential influencing factors. In consideration of the high co-linearity of these influencing factors, we used partial least squares regression (PLSR) to determine the associations between the stream nitrate concentration or flux and 26 selected watershed characteristics. The number of components was unequal for the nitrate concentration and flux models. The optimal models explained 66.4%, 60.0% and 59.9% of the variability in nitrate concentration and 74.7%, 67.1% and 58.0% of the variability in nitrate flux annually, in the dry season, and in the wet season, respectively. According to the variable importance in the projection (VIP) values, the dominant first-order factors for the nitrate concentration were as follows: the areal percentages of agricultural, forest and residential areas; followed by the slope; the largest patch index (LPI); the flow path gradient (FPG); the slope gradient variance (SGV); and the splitting index (SPLIT). In addition to these factors, the runoff coefficient (RC), flashiness index (FI), and patch density (PD) affected the changes in the nitrate flux. This study illustrates the influence of hydrological and environmental factors on seasonal water quality and can serve as guidelines for better watershed modeling and effective water quality management.

1. Introduction

Nitrate pollution has been identified as a crucial trigger for the deterioration of water quality and a major cause of eutrophication. Nitrate exports from diffuse sources represent a main concern for surface water management in agricultural areas (Menció et al., 2011; Huang et al., 2012). Multiple factors, including precipitation, physiographic conditions and landscape heterogeneity, can alter runoff generation and nutrient transport (Ekholm et al., 2000; King et al., 2005; Gardner and McGlynn, 2009). Previous study have selected a number of parameters to develop process-based nutrient export models across a range of scales, particularly in cases with few observation (Xiao and Ji, 2007; Zhou et al., 2012). Therefore, understanding the factors that affect nitrate concentration and flux is critical for developing nitrate export models, which are necessary to effectively target pollution mitigation and remediation.

The hydrological process is an important mechanism that explains the seasonal variation in water quality in a watershed (Ouyang et al., 2006). Nutrients are temporarily stored in the ground surface water, the vadose zone or the groundwater and then transported into the stream via subsurface water or surface runoff that is induced by precipitation (Laurent and Mazumder, 2014). The nutrient concentration peaks during flow peaks are referred to as first flush effects, whereas the concentration troughs during flow peaks are referred to as dilution effects (Kang et al., 2008; Billy et al., 2013). During dry periods, nutrients are stored in the vadose zone, and preferential flow cannot efficiently remove

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* Corresponding author at: College of Resources and Environment, Huazhong Agricultural University, Wuhan 430070, China
E-mail address: shizhihua70@gmail.com (Z.H. Shi).

http://dx.doi.org/10.1016/j.jhydrol.2016.12.015
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these stored nutrients. Intense rainfall events cause the percolation of soil pore water, and the leaching process may contribute to increasing nutrient concentration when the dilution effect of rainfall is not significant (Cao et al., 2004; Menció et al., 2011).

Stream water quality is indirectly influenced by watershed environmental conditions (e.g., land use, terrain, soil, and vegetation) via hydrological pathways (Uuemaa et al., 2005; Ouyang et al., 2010; Zhou et al., 2012). Land use patterns affect energy flow and runoff processes via hydrological pathways and therefore impact multiple hydrological and ecological functions (Turner, 1989; Rui et al., 2014). Topographical characteristics affect the nutrient transportation pathway (Chang, 2008). For example, a higher slope variability leads to higher discharge and erosion rates and increases the amount of nutrients entering the watershed (Sliva and Williams, 2001). Soil conditions determine the runoff distribution, and increasing non-point source pollution in the impervious area has been confirmed to be attributable to greater surface runoff (Tong and Chen, 2002; Neary et al., 2009). An increase in the vegetation cover contributes to water infiltration, subsequently decreasing the potential for soil erosion and nutrient loss (White and Greer, 2006). In contrast, land use types reflect the characteristics of human activity, which determine the hydrological system's input source and directly impact water quality (Lee et al., 2009). Previous studies have often focus on the composition of land cover within the watershed to explain variations in nutrient. Excessive nitrogen inputs from sources such as fertilizer or manure application during intensive agriculture and domestic wastewater from residential areas have been identified as major contributors to stream nitrogen loading (Berka et al., 2001; Massoud et al., 2006; Rui et al., 2014). Conversely, forest areas exhibit reduced surface runoff and provide protection from nutrient flow because of their extensive, deep root systems and their high-permeability soils (Neary et al., 2009).

The Danjiangkou Reservoir is the water source for the Middle Route Project under the South-to-North Water Transfer Scheme. Agricultural non-point source pollution has been identified as a major source of the contaminants that currently limit water quality in this region (Hao et al., 2012; Liu et al., 2012). Our investigation focused on nitrate because it comprises the largest fraction of total dissolved nitrogen in the study area (Luo et al., 2010). Upstream and downstream nitrate exports are interconnected; in addition, the watershed physiographic and landscape characteristics are highly co-linear or co-dependent (Shi et al., 2013; Yan et al., 2013). Partial least squares regression (PLSR) is a recently developed technique that can handle highly correlated datasets (Carrascal et al., 2009; Abdi, 2010). Long-term field monitoring series provide representative and reliable estimates of water quality and avoid the extensive parameterization and calibration that are involved in many process-based models (Dixon and Chiswell, 1996; Heathwaite, 2003). We established 15 sampling sites in the main stream and tributaries of the Hujiashan watershed and conducted biweekly sampling during 2008–2012 to monitor the nitrate exports. The objectives of this study were to (i) identify the seasonal patterns in nitrate exports using the available monitoring dataset and (ii) apply PLSR in a watershed to address how nitrate exports are related to the topography, land use composition and pattern, and hydrological properties.

2. Materials and methods

2.1. Study area

The Danjiangkou Reservoir is located on the Han River, the largest tributary of the Yangtze River, and is the water source for the Middle Route Project under the South-to-North Water Transfer Scheme initiated to overcome the spatially uneven water resource distribution in China (Piao et al., 2010). This reservoir supplies 13.8 billion m^3 of water annually to the northern regions (Shi et al., 2013). Thus, ensuring the water quality of the reservoir is an important topic for local and national policy makers.

The Hujiashan watershed covers 2256.9 ha and is located approximately 5 km from the Danjiangkou Reservoir (Fig. 1). It is characterized by a bedrock geology of Tertiary red sandstone. According to the Chinese soil classification system, the major soil types within this watershed include yellow-brown soil and purple soil (National Soil Survey Office, 1992), which correspond to Alfisols and Inceptosols, respectively, in the USA Soil Taxonomy (Soil Survey Staff, 1999). The watershed has a typical subtropical monsoon climate with a mean annual air temperature of 16.1 °C. The annual rainfall varies between 503 and 1360 mm, and the mean annual rainfall is 798 mm, of which more than 75% falls during the monsoon season (June to October). The elevation in the watershed ranges from 260 m in the south to 690 m in the north. The Hujiashan watershed contains 47.1% agricultural land, 40.8% forest, and 2.1% residential area. The major farming activities are wheat (*Triticum aestivum* L.) and corn (*Zea mays* L.) rotation, with wheat grown during the cold season and corn during the warm season.

2.2. Stream water sampling and chemical analysis

In this study, 15 sampling sites were established in the watershed (Fig. 1), and biweekly sampling was conducted during 2008–2012. The spatial distribution of the watershed nitrate concentration was investigated via synoptic sampling. Stream water was collected in 1-L high-density polyethylene (HDPE) bottles from each of 15 sites over a 2-h period. Moreover, 2–3 intensive sampling events (2-h intervals) were conducted during rainstorms every year. This intensive sampling during high-flow periods was used to reliably determine the relationship between concentration and discharge at various flow rates.

Water samples collected from the streams were transported to the laboratory and stored at 4 °C. They were filtered within 24 h of collection using 0.7-mm glass microfiber (GF/F) filters. Filtered water samples were preserved in HDPE bottles at 0–4 °C until analysis. The nitrate, nitrite and ammonium contents were determined by ion chromatography (IC) using a Dionex ICS-1500 instrument with detection limits of 0.2, 0.2, and 0.4 μm, respectively. The nitrite and ammonium concentrations of almost all of the samples were below the detection limit and were therefore not considered further. Nitrates were the dominant dissolved inorganic nitrogen species. To identify seasonal patterns of nitrate concentration, the datasets were divided into the wet season, i.e., May-October, and the dry season, i.e., November to the following April (Lin et al., 2011).

2.3. Ungauged subwatershed discharge

One gaging station was installed at the watershed outlet (Fig. 1). A hydrologic modeling approach was adopted to estimate the discharge at the ungauged sites. TOPMODEL, a semi-distributed, variable-source, topographically based hydrological model was selected for this study (Hornberger et al., 1994). The rainfall characteristics of the entire watershed were considered to be adequately represented by the data collected from the single weather station in the study area. The water discharge values during 2007–2009 at sampling site 10 were used for calibration, and the 2010–2012 data were used for validation. The performance of the model in simulating the water discharge was evaluated according to the Nash–Sutcliffe efficiency (E_{NS}) values: