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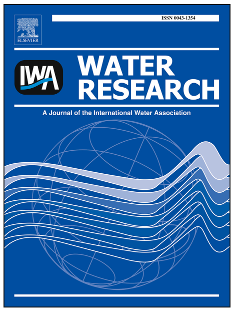

Spatiotemporal Patterns and Source Attribution of Nitrogen Load in a River Basin with Complex Pollution Sources

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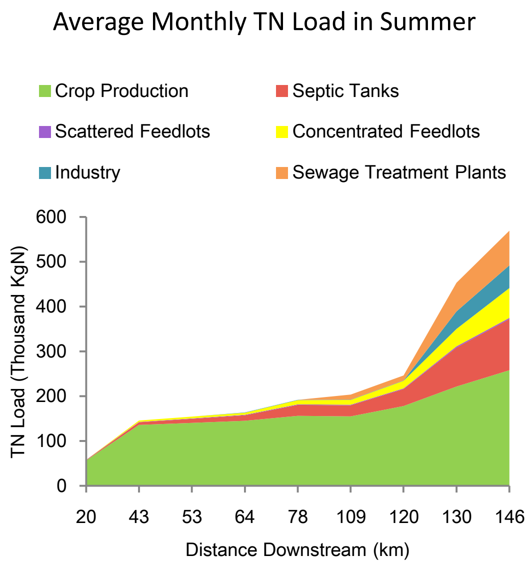
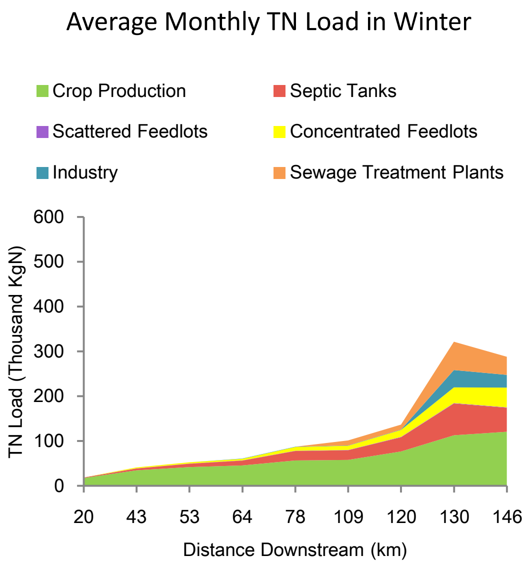


Average Monthly TN Load in Summer
Crop Production
Septic Tanks
Scattered Feedlots
Concentrated Feedlots
Industry
Sewage Treatment Plants
TN Load (Thousand KgN)
0
100
200
300
400
500
600
20
43
53
64
78
109
120
130
146
Distance Downstream (km)



Average Monthly TN Load in Winter
Crop Production
Septic Tanks
Scattered Feedlots
Concentrated Feedlots
Industry
Sewage Treatment Plants
TN Load (Thousand KgN)
0
100
200
300
400
500
600
20
43
53
64
78
109
120
130
146
Distance Downstream (km)

Spatiotemporal Patterns and Source Attribution of Nitrogen Load in a River Basin with Complex Pollution Sources

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ABSTRACT

Environmental problems such as eutrophication caused by excessive nutrient discharge are global challenges. There are complex pollution sources of nitrogen (N) discharge in many river basins worldwide. Knowledge of its pollution sources and their respective load contributions is essential to developing effective N pollution control strategies. N loads from all known anthropogenic pollution sources in the Upper Huai River basin of China were simulated with the process-based SWAT (Soil and Water Assessment Tool) model. The performances of SWAT driven by daily and hourly rainfall inputs were assessed and it was found that the one driven by hourly rainfall outperformed the one driven by daily rainfall in simulating both total nitrogen (TN) and ammonia nitrogen (NH_4-N) loads. The hourly SWAT model was hence used to examine the spatiotemporal patterns of TN and NH_4-N loads and their source attributions. TN load exhibited significant seasonal variations with the largest in summer and the smallest in spring. Despite its declining proportion of contribution downstream, crop production remained the largest contributor of TN load followed by septic tanks, concentrated animal feedlot operations (CAFOs), municipal sewage treatment plants, industries, and scattered animal feedlot operations (SAFOs). There was much less seasonal variation in NH_4-N load. CAFOs remained the largest source of NH_4-N load throughout the basin, while contributions from industries and municipal sewage treatment plants were more evident downstream. Our study results suggest the need to shift the focus of N load reduction from "end-of-pipe" sewage treatment to an integrated approach emphasizing stakeholder involvement and source prevention.

KEY WORDS

nitrogen load, spatiotemporal pattern, pollution source attribution, SWAT, hourly rainfall, Huai River

1. Introduction

Nitrogen (N) is arguably the most important nutrient in regulating primary productivity and species diversity in both aquatic and terrestrial ecosystems (Vitousek *et al.*, 2002). The ecological implications of human alterations to the N cycle have been profound as human activities have already significantly altered the global N cycle. From 1860 to the early 1990s, anthropogenic creation of reactive N compounds increased globally from approximately 15 to 156 Tg N y^{-1} (Galloway *et al.*, 2004). Human conversion of N_2 to more reactive N species has caused a wide range of environmental problems, ranging from effects on atmospheric chemistry, deterioration of freshwater quality, marine eutrophication, to declines in biodiversity (Henriksen *et al.*, 1997; Howarth, 2008; Pastuszak *et al.*, 2014).

The intensity and spatial variation of N loads into river basins depends on a number of natural as well as anthropogenic factors. The natural factors include land use/land cover types, soil types, meteorological, geological, hydrological conditions, and etc. The anthropogenic factors include emissions from various pollution sources, the operating pollutant removal facilities, and the implemented best management practices (Lepisto et al., 2006; Pastuszak et al., 2014; Gallo et al., 2015). The various rates, frequencies, and locations of N discharge as well as the diverse influencing factors of N transport and transformation make it very challenging to quantify each pollution source's N load contributions, especially in those river basins with complex pollution sources but limited data on pollution sources and N concentrations in water environment.

China is faced with the severe challenge of widespread eutrophication due to the excessive discharge of nutrients such as N. Many studies as well as its first national pollution census have indicated that non-point source pollution has played an increasingly significant role in water quality deterioration in China (Xu *et al.*, 2009; Liu *et al.*, 2013; Li *et al.*, 2014). Previous studies on non-point source pollution have been mostly focusing on agricultural runoff (Duncan, 2014; Guo *et al.*, 2014; Panagopoulos *et al.*, 2014; Yun *et al.*, 2015). Nevertheless, the composition of non-point pollution sources is usually more complex (Li *et al.*, 2014). In China, for example, more than 50 percent of its 1.3 billion population live in rural areas, where domestic sewage from rural households is hardly treated before being discharged into the environment. In addition, with rapid economic development and the subsequent improvement in people's living standards, there is an ever-growing appetite for meat and dairy consumption in the country. In response to this are the burgeoning animal feeding operations of different sizes, many of which are not equipped with sufficient waste disposal facilities.

River Huai, the third longest river in China, is one of the mostly polluted rivers in the country. During the past two decades, Chinese government has made tremendous investment to reverse the trend of deteriorating water quality in the basin, including 16.6 billion RMB on industrial sewage treatment between 1996 and 2000, and 25.6 billion RMB on municipal sewage treatment between 2001 and 2005. Since 2006, the government's focus has shifted from reducing the concentrations of discharging pollutants to reducing their total loads from the sources, with more than 60 billion RMB spent on cutting pollutant loads in the basin. However, the enormous financial investment has yet to bring about the much anticipated improvement in the water quality of the basin. For example, five categories of water bodies have been specified in the Chinese Surface Water Quality Standard (GB3838-2002). Among them, Category IV water could only be used for industrial production or human amusement without direct body contact, while Category V water could only be used for agriculture or scenery. The 2013 annual report of China's environment quality conditions by Chinese

Ministry of Environment Protection stated that water quality fell between category IV and V of the National Surface Water Quality Standard (GB 3838-2002) at 34.7% of the 95 routine monitoring sites along the River Huai, and below Category V at 17.9% of the monitoring sites.

Knowledge of pollution sources and their respective load contributions is the prerequisite to the development of cost-effective pollution control programs and optimization of pollution control strategies (Lindgren *et al.*, 2007; Carpenter, 2008) in a river basin. The pollution sources can be very complex that include rural households, crop production, animal feedlot operations, municipal sewage treatment plants, and industries. Previous studies have been mostly resorting to a variety of empirical coefficient methods to estimate pollution loads from various sources (Chen *et al.*, 2013; Liu *et al.*, 2013; Shen *et al.*, 2013; Delkash *et al.*, 2014). Not only is it difficult to validate the adopted empirical coefficients, the coefficient methods also fail to account for the migration and transformation of the pollutants from the points of discharge to the final receiving water bodies.

A number of dynamic process-based models such as the Soil and Water Assessment Tool (SWAT) (Arnold et al., 2014; Gassman et al., 2014) , the Hydrological Simulation Program–FORTRAN (HSPF) (Nasr *et al.*, 2007; Xie and Lian, 2013), the Integrated Nutrients in Catchments-Nitrogen (INCA-N) model (Rankinen et al., 2006; Wade et al., 2006), the Annualized Agricultural Nonpoint Source (AnnAGNPS) model (Pease *et al.*, 2010; Que *et al.*, 2015), and the HBV-NP (Andersson *et al.*, 2005; Lindstrom *et al.*, 2005) have been developed and used for modeling N loads in river basins. SWAT is selected in this study due to its open source feature and wide user communities, as well as its ability for simulating the pollutant transport processes from various point and non-point pollution sources in a river basin. Nevertheless, SWAT has been predominantly used to study non-point source pollution from agricultural fields (Zhang *et al.*, 2013; Cerro *et al.*, 2014; Jiang *et al.*, 2014; Ouyang *et al.*, 2014; Zhang *et al.*, 2014) despite its capabilities of incorporating a variety of pollution sources such as point sources and septic tanks (Oliver *et al.*, 2014). The ignorance of the point sources and septic tanks in the process-based models may lead to the overestimation of the relative contributions from diffusive sources such as agriculture and the disproportional targeting of potential pollution sources (Withers *et al.*, 2012).

The majority of water quality modeling studies, including those using SWAT, have used monthly or daily meteorological inputs to drive the models. However, meteorological inputs at different temporal resolutions, especially precipitation, could result in different simulations of hydrological responses and hence pollutant transport and transformation processes (Yang *et al.*, 2015). There is a need for deeper understandings of the impacts of the temporal resolution of precipitation on the process-based models' simulations of pollutant transport and transformation processes. In view of the gaps, the research objectives of this study are to (1) establish the SWAT model to simulate the N discharge and transport processes from all known anthropogenic point and non-point pollution sources in a river basin with complex pollution sources, (2) compare the SWAT models with daily and hourly rainfall inputs in their N pollution simulation performances, and (3) quantify the N load contributions from each pollution source and analyze their spatiotemporal patterns in a river basin.

This study differs from previous works using SWAT to simulate N loads in the following ways:

1. We used SWAT to simulate N discharge and transport processes from all known anthropogenic sources in a large river basin including crop production, scattered small-scale animal feedlot operations, rural household septic tanks,

industries, municipal sewage treatment plants, and concentrated animal feedlot operations.

2. We evaluated the impacts of the temporal resolution of rainfall inputs on the SWAT models' performance in both stream discharge and N load simulations in a large river basin.
3. We analyzed the spatiotemporal patterns of both total nitrogen (TN) and ammonia nitrogen (NH_4-N) load contributions from each of the six pollution sources. Each pollution source's seasonal TN and NH_4-N load contributions were analyzed and compared at nine locations along the main reach of the study region.

2. Materials and methods

2.1. Study region

The Ru River Basin lies upstream of the Huai River Basin and is selected as the study region. The River Ru originates from the Banqiao reservoir and runs for approximately 223 km passing through nine counties and one district of the Zhumadian City. The outlet of the Ru River Basin is located at the Shakou hydrological station. The study region completely falls within the administrative boundary of the Zhumadian City with a drainage area of 5803 km^2 (Fig. 1).

The study region is predominantly agricultural with farmland, wood land, grassland, and rural residential areas accounting for 65.6%, 14.5%, 5.1%, and 8.7% of its land coverage, respectively. Mostly hilly in the west and flat in the east, its surface elevation ranges from less than 50 m to nearly 1000 m. Located in the transition zone between the northern subtropical climate and warm temperate climate, the region has four distinctive seasons with annual mean temperature around 15℃ and precipitation around 900 mm. Heavily influenced by monsoon, precipitation in the region mostly occurs in the summer months from June to August.

Due to its favorable weather conditions and large extent of flat terrain, the region has traditionally been a main supplier of grain and meat products in China. In 2010, for example, the city of Zhumadian was reported to have a rural population of 5.08 million, producing 6.49 million tons of grains and 0.78 million tons of meat. Meanwhile, the city has substantial industrial activities with a gross industrial product value of 39.3 billion RMB in 2010. The industrial, agricultural, and domestic activities have contributed to significant water quality deterioration in the region. The water quality of the Banqiao reservoir, the origin of the River Ru, could meet the category III of the GB 3838-2002 Standard, allowing it to serve as a drinking water source for the local community. At the downstream Shakou hydrological station, however, its water quality deteriorates sharply. With annual mean total nitrogen (TN) concentration increasing to 3.93 mg/l in 2010, it even fails to meet the category V of the Standard. Understanding how various pollution sources contribute to the considerable increase in N concentration is the prerequisite to developing effective water pollution control programs in the region.

2.2 Data Sources

The land use and land cover (LULC) data in 2005 was obtained from the Chinese Academy of Sciences, which was further classified into the standard LULC categories of SWAT. The soil types and properties were mostly extracted from the soil databases of Nanjing Institute of Soil Science (Yu *et al.*, 2007a; Yu *et al.*, 2007b; Shi *et al.*, 2010), except that the available water capacity and soil carbon content were estimated using the SPAW (Soil – Plant – Atmosphere – Water) software (Saxton and Willey, 2005), and the soil nutrient contents (nitrate, organic nitrogen, labile phosphorous, and organic phosphorous) were obtained from the local soil survey reports. Table 1 summarized the required data inputs for the SWAT model and their sources.

The 25m Digital Elevation Model (DEM) data was used to delineate the sub-basins. With a threshold area of 8000 ha, a total of 55 sub-basins were delineated (Fig. 1), which were further divided into 394 hydrological response units (HRUs). Each HRU represents homogeneous characteristics of LULC, soils, and slopes. The residential medium/low density (URML) areas that represent rural residential areas were all retained during HRU delineation for simulating N load from rural septic tanks.

Daily records of maximum and minimum temperature, sunshine hours, relative humidity, and wind speed at the Zhumadian weather station from 2001 to 2011 were acquired from the China Meteorological Administration. Daily sunshine hours were converted to daily solar radiation using the Angstrom-Prescott equation (Prescott, 1940) with empirical parameters from Zuo et al. (1963). Daily and hourly rainfalls at 28 rainfall stations from 2001 to 2011 were obtained from the Hydrological Yearbooks compiled by the Ministry of Water Resources of China. Daily streamflows and the subsequently derived monthly streamflows at three hydrological stations (Lixin, Luzhuang, and Shakou) and daily outflow from three major reservoirs (Banqiao, Boshan, and Suyahu) from 2005 to 2011 were also obtained from the reports (see Fig. 1 for the locations of the three stations and reservoirs).

Monthly observations of TN and ammonia nitrogen (NH_4-N) concentrations at the Shakou station from 2006 to 2011 were obtained from the Bureau of Environmental Protection of the Zhumadian City. Between 2006 and 2008, TN concentrations were only monitored in the odd numbered months. Monthly TN and NH_4-N concentrations were multiplied by monthly streamflows to estimate their monthly loads, respectively. Both point and non-point pollution sources are responsible for the deteriorating water quality in the study region. Point sources include industries, municipal sewage treatment plants, and concentrated animal feedlot operations (CAFOs). Non-point pollution sources include crop production, scattered small-scale animal feedlot operations (SAFOs), and rural households. Annual N emissions from industries and CAFOs were extracted from the database of 2010 census of pollution sources in the Zhumadian City. N emissions from six municipal sewage treatment plants in 2010 were obtained from the Bureau of Environmental Protection of the Zhumadian City. Total N emissions from industries, CAFOs, and municipal sewage treatment plants were summarized for the 21 sub-basins with the presence of point sources (Fig. 1), and their mean monthly loads were used as point source inputs in SWAT.

Face-to-face interviews with 116 randomly selected farmers from 16 villages in the study region were conducted to collect information on current crop management practices. Our interview results indicated that most of the agricultural fields in the region were under the wheat-corn rotation (June to September for growing corn and October to next May for growing wheat) with fairly homogeneous crop management practices as summarized in Table 2.

Rural population of the nine counties and one district located fully or partially in the study region was obtained from the Statistical Yearbook of the Zhumadian city. The rural population density of each sub-basin was estimated as the area-weighted average of county rural population densities, based on which the rural population of its HRUs containing URML was calculated.

Like many other regions in China, rural domestic sewage has not been collected for central treatment in the study region. Conventional septic tanks are the main facilities for rural sewage treatment. Based on previous studies of the characteristics of rural household sewage discharge and the pollutant removal efficiencies of septic tanks in China, the septic tank effluent flow rate was set to be 50 l/d per capita, and the TN concentration of the septic tank effluent was set to be 90 mg/l in the SWAT model

(WANG *et al.*, 2008; Xu *et al.*, 2008; WANG *et al.*, 2010; Hou *et al.*, 2012).

County level N emissions from SAFOs in 2010 were obtained from the Bureau of Animal Husbandry of the Zhumadian City, which was converted to the equivalent amount of pig manure based on the average ammonia content of 2.57%. N loads from SAFOs were estimated by assuming that the equivalent amount of pig manure was applied uniformly to crop fields within each county. Each sub-basin's pig manure application rate was estimated as the area-weighted average of the county application rates.

2.3 SWAT Model Development

Both daily and hourly rainfall data were used as inputs for the SWAT models and their performances in discharge and N load simulations were compared. The SWAT models driven by daily and hourly rainfall are hereinafter referred to as the daily SWAT model and the hourly SWAT model, respectively. The Soil and Water Assessment Tool Calibration and Uncertainty Procedure (SWAT-CUP) (Abbaspour, 2011) program was used for the calibration and validation of the SWAT models. The Nash-Sutcliffe model efficiency (NSE) coefficient (Nash and Sutcliffe, 1970) and the coefficient of determination (R^2) are used as the objective function (see Equations 1 and 2) to evaluate the model performance.

$$NSE = 1 - \frac{\sum_{i=1}^{n}(Y_i^{obs} - Y_i^{sim})^2}{\sum_{i=1}^{n}(Y_i^{obs} - \overline{Y^{obs}})^2} \qquad (1)$$

$$R^2 = \frac{\left[\sum_{i=1}^{n}\left(Y_i^{obs} - \overline{Y^{obs}}\right)\sum_{i=1}^{n}\left(Y_i^{sim} - \overline{Y^{sim}}\right)\right]^2}{\sum_{i=1}^{n}\left(Y_i^{obs} - \overline{Y^{obs}}\right)^2\sum_{i=1}^{n}\left(Y_i^{sim} - \overline{Y^{sim}}\right)^2} \qquad (2)$$

where: n is the total number of observations, Y_i^{obs} is the value of the observed variable at the ith time-step, Y_i^{sim} is the value of the simulated variable at the ith time-step, and $\overline{Y^{obs}}$ and $\overline{Y^{sim}}$ are the mean of the measured and simulated values.

Ranging from 0 to 1, R^2 indicates the percentage of variance in measured data accounted for by the variance in the simulated results. NSE is a normalized statistic that describes the degree of the ‘goodness-of-fit’ between model predictions and observations and can vary between -∞ and 1, where a value of 1 represents a perfect fit. It needs to be noted here although the models were driven by daily or hourly precipitation, their performances of discharge and N load simulations were evaluated at a monthly time step. Moriasi *et al.* (2007) suggested that the SWAT model evaluated at a monthly time step should achieve an NSE value of 0.5, 0.65, and 0.75 to be considered as “satisfactory”, “good”, or “very good”, respectively.

The SWAT models were calibrated in two steps. The model parameters associated with discharge simulations were calibrated first, followed by those associated with N load simulations. The SUFI-2 algorithm built in the Soil and Water Assessment Tool Calibration and Uncertainty Procedure (SWAT-CUP) (Abbaspour 2011) was used for both the calibration and validation of the SWAT models with several iterations of 1000 simulations. In discharge simulation , after the warming-up period from 2001 to 2004, the SWAT model was calibrated from 2005 to 2007 and validated from 2008 to 2011 based on the monthly streamflow records at the Lixin, Luzhaung, and Shakou hydrological stations. In N load simulation, both TN and NH_4-N loads at the Shakou station were used. Because N emissions from many pollution sources were only available for 2010, the SWAT models for N load simulations were only calibrated for the period between 2006 and 2011 when monthly TN and NH_4-N concentration data were available.

2.4 Source Attribution of N Loads

Multiple runs of the SWAT model with different scenarios of pollution source inputs were conducted to estimate the amount of N load from individual pollution source. As the baseline scenario, the SWAT model was first run without any pollution source except fertilizer applications on crop fields to estimate the N load from crop production, denoted as $Load_{crop}$. For the other five point and non-point pollution sources, different SWAT model runs were then carried out to estimate the combined N loads from crop production and each individual pollution source, whose difference from the baseline scenario was calculated as the load from individual pollution source. For example, to calculate the N load from industries, the SWAT model was run only with industrial N emissions and fertilizer applications, which yielded an estimate of the combined N load from industries and crop production denoted as $Load_{crop+ind}$. N load contributed by industries could then be simply calculated as $Load_{crop+ind}$-$Load_{crop}$. The same procedures were repeated to estimate the N load from municipal sewage treatment plants, CAFOs, SAFOs, and septic tanks, respectively.

3. Results and discussion

3.1 Comparison of the daily and hourly SWAT models

Table 3 listed the initial range and the calibrated values of the parameters in the daily and hourly SWAT models for discharge simulation. At the beginning of the calibration, the same range was used in the calibration of both models. For the parameter *Alpha_BF*, its calibration bounding limits were estimated based on the historical daily discharge records of the hydrological stations using the baseflow filter program (Arnold and Allen 1999). Comparison between the calibrated daily and hourly models indicated that the differences in their parameters mainly lay in those related to surface runoff and groundwater. In the hourly model, its larger *CN2* values led to higher surface runoff potentials; its larger *GW_DELAY* value caused more delay for soil water to reach the shallow aquifer; and its larger *GW_REVAP* and lower *REVAPMN* values enabled more groundwater to diffuse upward and evaporate. These parameter differences seemed to indicate that the hourly model would predict more surface runoff and less baseflow contributions than the daily model. However, the two models yielded opposite water balance analysis results. The daily model gave an estimate of 39% baseflow contribution to streamflow compared to a larger estimate of 46% by the hourly model. The difference in water balance estimates could be due to the different runoff estimation methods used by the two SWAT models. The daily SWAT model used the SCS curve number method, while the hourly model used the Green & Ampt infiltration method. In addition, the baseflow filter program gave an estimate of 0.47 for baseflow contribution, which coincided more with the hourly model results.

Table 4 listed the initial range and the calibrated values of the parameters in the daily and hourly SWAT models for N load simulation. At the beginning of the calibration, the same range was used in the calibration of both SWAT models. Comparison between the calibrated values of the parameters of the two models showed that they mostly fell within a similar range.

Table 5 compared the performances of the daily and hourly SWAT models for simulating discharge and N loads in the study region. Both models were able to simulate monthly discharge at the three hydrological stations satisfactorily with the NSE coefficients all above 0.8 and R^2 all above 0.85 for both the calibration and validation periods. However, there was much difference in their simulations of monthly TN and NH_4-N loads. The NSE statistics of the hourly SWAT model for simulating TN and NH_4-N loads were both 0.82, much higher than 0.63 and 0.58 of the daily model. According to the criteria suggested by Moriasi et al. (2007), the hourly SWAT model achieved "very good" performance in simulating monthly TN and NH_4-N loads, whereas the performance of the daily model could only be considered as "satisfactory".

Fig. 2 compared the observed and simulated TN and NH_4-N loads by the daily and hourly SWAT models at the Shakou station for the time period 2006-2011. In general, the daily SWAT model tended to predict more TN and NH_4-N loads than the hourly model, which resulted in a lower NSE value. As shown in Table 4, there was not much difference in the calibrated values of the parameters directly related to N transport and transformation process between the daily and hourly SWAT models. The possible reason for the difference between the two models' simulations of N load could be due to their different representations of the hydrological processes in the study region. The hourly model estimated that baseflow contributed to about 46 % of the total flow, while the daily model gave an estimate of 39%. Likewise, the ratio of percolation to precipitation was estimated to be 0.28 in the hourly model, compared to 0.15 in the daily model. The higher estimate of the baseflow contribution by the hourly model meant that it predicted more N transport to rivers via the longer and slower path of soil percolation and groundwater movement, hence allowing more N removal than the shorter and faster path of surface runoff.

3.3 Spatiotemporal analysis and source attributions of N loads

The SWAT model driven by hourly rainfall outperformed the one driven by daily rainfall, and hence was used to analyze the spatiotemporal patterns of N loads and the contributions from various pollution sources. Average monthly TN and NH_4-N loads at nine sub-basin outlets located along the main reach of the Ru River were compared for each season (Fig. 3).

In the study region, TN load was the highest in summer followed by fall, winter, and spring, mainly due to the seasonal change in the load from crop production. At the upstream location close to the Banqiao reservoir (comparison point 1), the majority of the TN load was contributed by crop production, accounting for more than 70% in spring and more than 90% in the other seasons. The second largest pollution source is septic tanks, although with much less contribution than crop production, accounting for 29.2% of the TN load in spring and less than 5% in the other seasons. SAFOs contributed the remaining less than 1% of the TN load throughout the year (Fig. 4).

With increasing TN load contributions from other sources downstream, percentage of TN load from crop production decreased constantly although it remained as the largest contributor. At around a distance of 120 km downstream (comparison point 7) before the joining of the tributary of Lianjiang River, which flows through the heavily urbanized and industrialized Zhumadian urban area, crop production contributed around 70% of the TN load in summer and fall, 56.2% in winter, and 42.9% in spring. Septic tanks ranked as the second largest contributor of the TN load, accounting for 29.8% in spring, 23.1% in winter, and around 16% in fall and summer. CAFOs and municipal sewage treatment plants ranked the third and fourth in their TN load, which accounted for 15.0% and 10.4% in spring, 11.4% and 8.1% in winter, 8.1% and 5.8% in fall, and 6.8% and 4.6% in summer. Both industries and SAFOs accounted for less than 1% of the TN load throughout the year (Fig. 4).

At the outlet of the Ru river basin (comparison point 9), the percentage of TN load contributed by crop production dropped to 29.4% in spring, 45.3% in summer, 53.8% in fall, and 41.9% in winter. Septic tanks remained as the second largest polluter, contributing 22.8% in spring, 20.0% in summer, 14.8% in fall, and 18.6% in winter. TN loads from municipal sewage treatment plants and CAFOs were similar, contributing around 18% in spring, 15% in winter, and 12% in summer and fall. There was a large increase in the TN load from industries, accounting for 12.1% in spring, 8.9% in summer, 7.8% in fall, and 9.9% in winter. TN load from SAFOs remained below 1% throughout the year (Fig. 4).

The composition of pollution sources for NH_4-N load was very different from TN (Fig. 5). CAFOs replaced crop production to be the largest source of the NH_4-N load, followed by industries and municipal sewage treatment plants. Meanwhile, there was not as much seasonal difference in the NH_4-N load as in the TN load. At the upstream above the Banqiao reservoir, average monthly NH_4-N load fell below 200 KgN throughout the year. Before reaching around 120 km downstream, it increased gradually by receiving loads mainly from CAFOs and later municipal sewage treatment plants. At the distance of 120 km downstream (comparison point 7), over 70% of the NH_4-N load came from CAFOs, compared to around 22% from municipal sewage treatment plants, 2% from industries, and 1% from the remaining sources throughout the year. Afterwards, there was a sharp increase in the NH_4-N load from industries. At the outlet of the Ru River basin, CAFOs contributed 45.2% of the NH_4-N load in spring, 37.1% in summer, 45.4% in fall, and 49.5% in winter. Industries rose to the second largest source of NH_4-N load, contributing 30.2% in spring, 28.5% in summer, 26.3% in fall, and 26.7% in winter. Municipal sewage treatment plants ranked third in the NH_4-N load, contributing 24.5% in spring, 20.4% in summer, 23.4% in fall, and 23.6% in winter. Crop production contributed to the NH_4-N load mostly in summer and fall, accounting for 13.0% and 4.4%, respectively. Septic tanks and SAFOs remained as insignificant sources, contributing less than 1% throughout the year (Fig. 5).

3.4 Comparisons with previous N source attribution studies

Previous process-based modeling studies on N loads have been mostly focused on agricultural runoff, with some considering loads from municipal and industrial point sources, and few considering loads from septic tanks and animal feedlot operations. For example, Wu and Chen (2013) used SWAT to investigate the influence of point source (municipal and industrial sources) and non-point source (agriculture, atmospheric deposition, and plant residue decomposition) pollution on the water quality of the Dongjiang River in southern China, and they concluded that agriculture was the dominant source of N loads.

In contrast, quite a few N load studies utilizing export coefficient methods have encompassed more types of pollution sources. For example, Liu *et al.* (2013) estimated that rural residential sewage, animal feedlot operations, fertilizer applications, and industries accounted for 43%, 14%, 10%, and 7% of the N loads to the Lake Tai of Eastern China. Wang *et al.* (2013) estimated that rural residential sewage, agricultural activities (including crop production and animal feedlot operations), and industries accounted for 54%, 34%, and 4% of the TN loads and 66%, 24%, and 5% of the NH_4-N loads to the Lake Dianshan of Southern China. HAO *et al.* (2014) estimated that rural residential sewage, urban runoff, animal feedlot operations, and fertilizer applications contributed 35%, 36%, 18%, and 5% of the non-point source TN loads and 76%, 10%, 11%, and 1% of the NH_4-N loads to the River Shaying of Central China. In spite of the differences in their natural and socioeconomic conditions, rural residential sewage was identified as the largest contributor of TN and NH_4-N loads in all three basins, while animal feedlot operations and crop production activities were assessed to contribute moderately.

There have also been some studies that adopted an intermediate approach between the empirical coefficient methods and the process-based models to quantify N load contributions, For example, Wang *et al*. (2011) developed an ENPS_LSB (estimate non-point source pollutant loads in a large-scale basin) model to take into account the complex non-point pollution sources (agricultural fields, urban, rural residential, and livestock) in China. In this model, a number of factors such as transfer coefficient, natural correction factor, and social correction factor were introduced to correct the empirical export coefficients. Much different from the results of the aforementioned export coefficient studies, the application of the ENPS_LSB model in the Yangtze River Basin estimated that 76.8% of non-point source dissolved TN loads were from agricultural fields. Chen et al. (2013) coupled a land-use based export coefficient model, a stream nutrient transport equation, and the Bayesian statistics for stream N source apportionment in the River ChangLe watershed of Zhejiang Province. They estimated that paddy fields, dry farming land, residential lands, and forest land contributed approximately 22%, 49%, 11%, and 18% of TN load for the entire watershed, respectively.

In this study, we identified crop production as the largest source of the TN load in the study region followed by septic tanks. TN loads from CAFOs and municipal sewage treatment plants varied between the third and fourth place seasonally. As for the NH_4-N load, CAFOs, municipal sewage treatment plants, and industries were identified as the top three sources in the study region. Overall, our N load source attribution results are relatively consistent with previous studies that have incorporated nutrient transport in various ways, while much different from those studies purely based on export coefficients. One possible reason for the distinct difference between our study and those purely based on export coefficients is the incorporation of the N migration and transformation processes in the SWAT model. For example, although rural residential sewage may produce a large amount of TN and NH_4-N loads in the septic tanks due to the large rural population, they mostly migrated to the receiving water bodies through the long and slow process of groundwater movement, where many of which were reduced through physical, chemical, and biological processes. Failing to account for these N transport and transformation processes could easily make the export coefficient method over-estimate both the TN and NH_4-N loads from rural residential sewage.

In addition, stable nitrogen ($\delta^{15}N$) and oxygen ($\delta^{18}O$) isotope data have been used to identify N sources in surface and groundwater based on different sources' distinct isotopic characteristics worldwide (Xue et al. 2009). In China, based on their monitored ^{15}N and$\delta^{18}O$ values, Jin et al. (2015) concluded that the dominant sources of nitrate in surface water were soil nitrogen and chemical fertilizers in the West Lake watershed of eastern China. Ding et al. (2014) combined the dual isotope approach with a Bayesian model to identify diffusive nitrate sources in the Lake Taihu Basin of eastern China. They found that soil nitrogen and chemical fertilizers were the main source of nitrate throughout the year. Meanwhile, manure and sewage contributed 22.4% of nitrate during the dry season from October to April, compared to 17.8% in the rainy season from May to September. Using a similar approach in the ChangXing County of Zhejiang province, Yang et al. (2013) estimated that soil nitrogen and chemical fertilizers contributed approximately 71% of nitrate in surface water in May (wet season) compared to 24% by manure and sewage. Nevertheless, in December (dry season), they estimated that soil nitrogen and chemical fertilizers contributed around 38% compared to 54% by manure and sewage. This phenomenon of dominant contributions from soil nitrogen and chemical fertilizers in the wet season and increasing contribution proportions from manure and sewage in the dry season have also been reported in other regions of China, such as the Sanjiang Plain of northeastern China (Lu et al. 2015), the upper streams of Miyun Reservoir of northern China (Li et al. 2014), and the upper Yangtze River of southwestern China (Li et al. 2014), and they were consistent with our N load source attribution results in Fig. 4.

3.5 Implications to N pollution control

Five categories of water bodies have been specified in the Chinese Surface Water Quality Standard (GB3838-2002). Among them, category III water could be used for drinking, fishery, and swimming, while category V only for agriculture and scenery. Fig. 6 compared the observed monthly TN and NH_4-N concentrations at the Shakou Station between 2006 and 2011 with the Category III and V standards. Monthly NH_4-N concentrations could meet the Category III standard except during two months in the first half of 2006. Monthly TN concentrations, however, were unable to meet the Category III standard throughout the period. In fact, less than 30% of the TN observations were able to meet the Category V standard. This suggests that the imminent focus of N pollution control in the region should lie in the reduction of TN load.

Our N source attribution results have suggested the need of a significant shift in the focus of N load reduction from the reliance of "end-of-pipe" sewage treatment facilities to an integrated watershed approach emphasizing stakeholder involvement and source prevention in the study region. Large but scattered settlements in many rural areas of China require a significant amount of investment in rural sewage treatment. Despite the recent developments in onsite wastewater treatment technologies, there remain considerable challenges in establishing an efficient system for rural sewage collection as well as treatment facility maintenance in China. It is therefore very hard to achieve large amount of N load reductions from rural households in the near future. Meanwhile, there have been many reports of excessive fertilizer application in different parts of China (Peng *et al.*, 2009; Zhang *et al.*, 2011; Yang *et al.*, 2012; Yan *et al.*, 2013). Previous surveys of the farmers in vicinity have revealed a prevalent lack of training in fertilizer applications and implementation of better fertilization practices such as soil testing and using controlled release fertilizers, as well as a sharp decline in applying organic fertilizers (Yang and Fang, 2015). Considering its role as the largest TN load contributor and the prevalently inadequate fertilization practices, development of agricultural extension programs for encouraging better fertilization practices should be put in the top priority for reducing TN load in the region and possibly many other regions worldwide.

In addition, fixed locations and large operation scale made CAFOs another potential source for TN load reduction. The technologies of converting animal manure to biogas and organic fertilizers have been fairly mature (Nasir *et al.*, 2012). If designed and managed properly, the programs for reducing loads from CAFOs could not only reduce their TN load, but also mitigate the issue of lacking organic fertilizer applications in crop production. Therefore, developing sustainable agriculture programs and closing the nutrient loop in rural areas is the key to reducing TN load and improving water quality.

4. Conclusion

The presence of multiple point and non-point pollution sources in a river basin is prevalent worldwide. Knowledge of their individual pollution load contributions and spatial-temporal patterns is essential to the development of sound river basin water pollution control strategies and programs. This study used the process-based SWAT model to analyze the N load source attributions as well as their spatiotemporal patterns for all known anthropogenic pollution sources in the Upper Huai River Basin of China. Key findings of the work are as follows:

- The process-based modeling approach can give more reliable pollutant load estimates and source attributions than the conventional approach based on empirical coefficients because the latter cannot account for the migration and transformation of the pollutants from the points of discharge to the final receiving water bodies. Process-based models, therefore, should be used to simulate N loads from various sources whenever the required data is available.

- The SWAT model driven by hourly rainfall inputs can enhance the representation of the hydrological processes of the study region, especially the sub-surface processes where nitrogen removal processes mostly take place. It outperformed the one driven by daily rainfall inputs for simulating both TN and NH_4-N loads.
- TN loads exhibited distinctive seasonal patterns. In general, TN loads from crop production were the largest, followed by septic tanks, municipal sewage treatment plants, and CAFOs. There was less seasonal variation in NH_4-N loads. In general, NH_4-N loads from CAFOs were the largest, followed by industry, and municipal sewage treatment plants. Implementing sustainable agriculture programs for reducing loads from crop production and CAFOs and closing the nutrient loop in rural areas is the key to reducing TN load and improving water quality.

Eutrophication and other water problems caused by excessive nutrient discharge are issues of concern worldwide. Similar studies are very important to be undertaken for river basins in different parts of the world to help to estimate and prioritize the N loads from all anthropogenic pollution sources, and formulate the most appropriate strategies and programs for N pollution control. The model set up in this study can also be used to assess the impacts of land use and climate change on N loads and their uncertainties, and provide decision-support for the development of mitigation programs. In addition, due to limited water quality observations, we calibrated the SWAT models based on monthly TN and NH_4-N loads. In the future, water quality observations of higher temporal resolution (such as daily) could be used to derive more accurate contaminant load estimates for model calibration, better understand the temporal variability of contaminant loads from different pollution sources, and evaluate the impacts of climate change, especially extreme events, on contaminant loads and the associated

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uncertainties.

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Table 1. Data inputs for the SWAT model

Category	Data	Scale/Extent	Data Sources
Water Quantity	DEM	1:50,000	Chinese National Geomatics Center
	Land Use/ Land Cover (2005)	1:100,000	Chinese Academy of Sciences
	Soil types and soil properties	1:1000,000	Nanjing Institute of Soil Science; Henan Province Soil Survey Office (1995); SPAW software
	River networks	1:250,000	Chinese Academy of Sciences
	Daily weather (1960-2011)	1 station	China Meteorological Administration
	Daily and hourly rainfall (2001-2011)	28 stations	Ministry of Water Resources of China
	Monthly streamflow (2005-2011)	3 stations	Ministry of Water Resources of China
	Daily reservoir outflow (2005-2011)	3 reservoirs	Ministry of Water Resources of China
Water Quality	Annual N emissions from industries (2010)	74 river segments	2010 Census of Pollution Sources in the Zhumadian City
	Annual N emissions from CAFOs (2010)	74 river segments	2010 Census of Pollution Sources in the Zhumadian City
	Annual N emissions from municipal sewage treatment plants (2010)	6 sewage treatment plants	Bureau of Environmental Protection of the Zhumadian City
	Annual N emissions from SAFOs (2010)	9 counties and 1 district	Bureau of Animal Husbandry of the Zhumadian City
	Total rural population (2010)	9 counties and 1 district	Statistical Yearbook of the Zhumadian City
	Total crop planting areas (2010)	9 counties and 1 district	Statistical Yearbook of the Zhumadian City
	Crop management practices	116 farmers	Field Survey

Table 2. Crop management operations during the wheat-corn rotation

Crop	Year	Month	Day	Operations
Corn	1	6	4	Start growth season
	1	6	4	Apply compound fertilizers (750 kg/ha)
	1	6	4	Apply urea (187.5 kg/ha)
	1	7	6	Apply urea (150 kg/ha)
	1	9	30	Harvest
Wheat	1	10	7	Start growth season
	1	10	7	Apply compound fertilizers (750 kg/ha)
	1	10	7	Apply urea (93.75 kg/ha)
	2	2	10	Apply urea (93.75 kg/ha)
	2	6	1	Harvest

Table 3. Comparison of parameter values between the daily and hourly SWAT models for discharge simulation

Parameter	Description	Range	Calibrated Values	
			Daily Model	Hourly Model
SURLAG	Surface runoff lag coefficient	1-10	7.8	8.7
ALPHA_BF	Baseflow alpha factor	0.03-0.1	0.06	0.06
GW_DELAY	Groundwater delay	10-300	13.8	265.1
GWQMN	Threshold depth of water in the shallow aquifer required for return flow to occur	10-150	26.7	72.8
REVAPMN	Threshold depth of water in the shallow aquifer for "revap" to occur	10-200	134.2	18.6
GW_REVAP	Groundwater "revap" coefficient	0.02-0.2	0.02	0.15
CANMX_AGRR	Maximum canopy storage of agricultural land	1-10	1.4	1.3
CANMX_URML	Maximum canopy storage of medium/low density residential areas	1-10	0.3	2.4
EPCO	Plant uptake compensation factor	0.85-1	0.90	0.91
ESCO	Soil evaporation compensation factor	0.85-1	0.87	1.00
CN2_AGRR	Moisture condition II curve number for agricultural land	67-99	69-91 [a]	76-98
CN2_URML	Moisture condition II curve number for medium/low density residential areas	62-92	60-75 [a]	75-90
CH_N2	Manning's "n" value for the main channel	0.035-0.049	0.045	0.042
CH_K2	Effective hydraulic conductivity in main channel alluvium	0-50	6.6	4.9
SOL_AWC	Available water capacity of the soil layer	0.12-0.36	0.15-0.35 [b]	0.15-0.35
SOL_K	Saturated hydraulic conductivity of the soil layer	1.6-901.3	1.9-862.8 [b]	1.9-864.0
CH_N1	Manning's "n" value for the tributary channels	0.19-0.32	0.27	0.24
CH_K1	Effective hydraulic conductivity in tributary channel alluvium	0-50	3.7	0.9

[a] Show the range of the calibrated values for different hydrological groups.

[b] Show the range of the calibrated values for different soil types and soil layers.

Table 4. Comparison of parameter values and sensitivities between the daily and sub-daily SWAT models

Parameter	Description	Range	Calibrated Values	
			Daily Model	Hourly Model
CDN	Denitrification exponential rate coefficient	0-3	2.38	2.22
CMN	Rate factor for humus mineralization of active organic nitrogen	0.001-0.003	0.0018	0.0013
NPERCO	Nitrogen percolation coefficient	0-1	0.1	0.1
RSDCO	Residue decomposition coefficient	0.02-0.1	0.08	0.06
ERORGN	Organic N enrichment ratio	0-5	0.28	0.69
COEFF_DENITR	Denitrification rate coefficient	0.1-50	14.2	37.9
COEFF_NITR	Nitrification rate coefficient	0.1-300	20.4	83.5
BC1	Rate constant for biological oxidation of NH4 to NO2 in the reach at 20°C	0.1-1	0.81	0.98
BC3	Rate constant for hydrolysis of organic N to NH4 in the reach at 20°C	0.02-0.4	0.33	0.27
RS1	Local algal settling rate in the reach at 20°C	0.15-1.82	0.99	0.60
RS4	Rate coefficient for organic N settling in the reach at 20°C	0.001-0.1	0.08	0.07
AI0	Ratio of chlorophyll-a to algal biomass	10-100	52.66	55.40
K_N	Michaelis-Menton half-saturation constant for nitrogen	0.01-0.3	0.09	0.17
MUMAX	Maximum specific algal growth rate at 20°C	1-3	2.27	2.88
P_N	Algal preference factor for ammonia	0-1	0.88	0.59
RHOQ	Algal respiration rate at 20°C	0.05-0.5	0.10	0.37

Table 5. Comparison of model evaluation statistics between the daily and hourly SWAT models for discharge and N load simulations

Station	NSE				R^2			
	Calibration		Validation		Calibration		Validation	
	Daily	Hourly	Daily	Hourly	Daily	Hourly	Daily	Hourly
Discharge								
Lixin	0.92	0.86	0.84	0.94	0.92	0.89	0.93	0.97
Luzhuang	0.85	0.82	0.84	0.83	0.89	0.94	0.87	0.87
Shakou	0.98	0.93	0.95	0.98	0.99	0.96	0.98	0.98
TN load								
Shakou	0.63	0.82	--	--	0.77	0.87	--	--
NH_4-N load								
Shakou	0.58	0.82	--	--	0.80	0.84	--	--

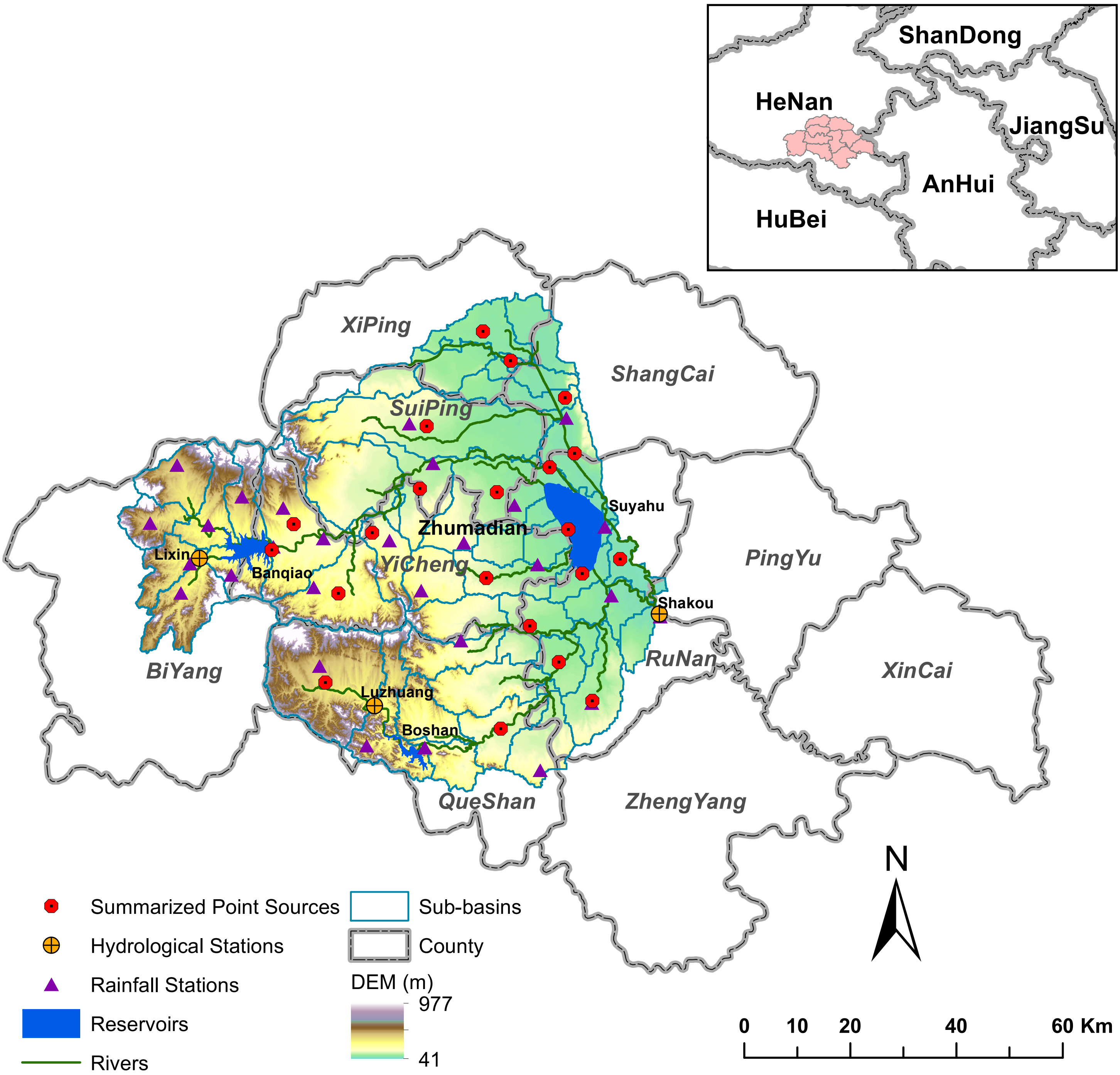
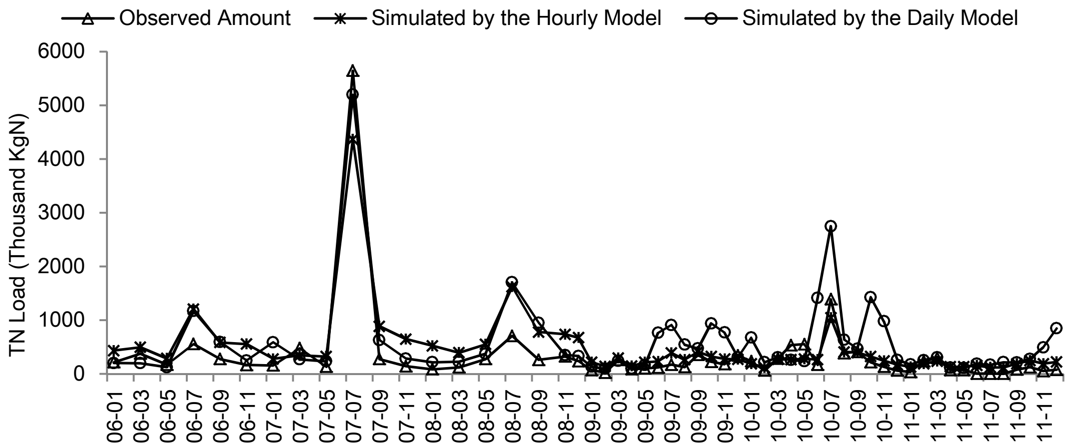
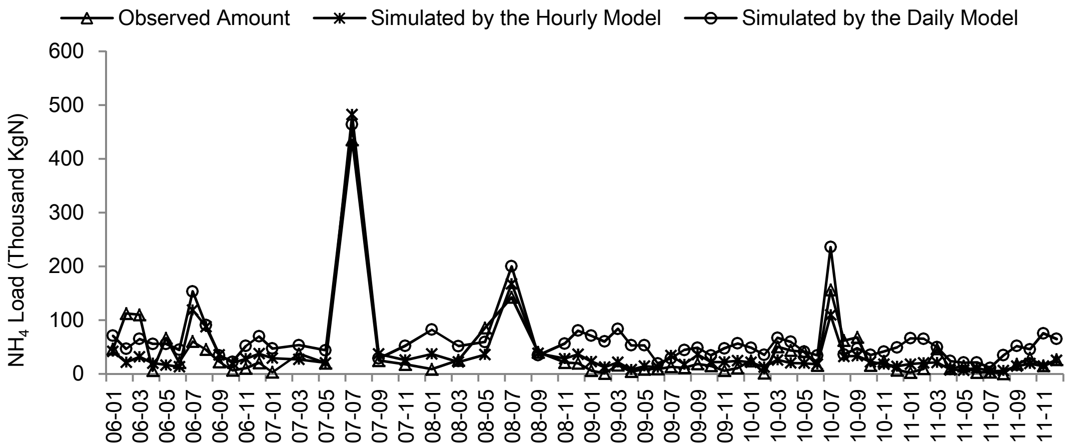


Fig. 1 - The map of the study region. Out of 55 sub-basins, 21 of them have point sources of N. The location of the administrative boundary of the Zhumadian City overlapped on the map of adjacent provinces is shown in the upper right panel.



(a) TN



(b) NH_4-N

Fig. 2. The observed and simulated amount of monthly N loads by the daily and hourly SWAT models for the period 2006-2011 at the Shakou station: (a) TN; (b) NH_4-N

ID	Downstream Distance (km)	Contribution Area (km^2)
1	20	333
2	43	1069
3	53	1323
4	64	1436
5	78	1806
6	109	1821
7	120	2330
8	130	4481
9	146	5803

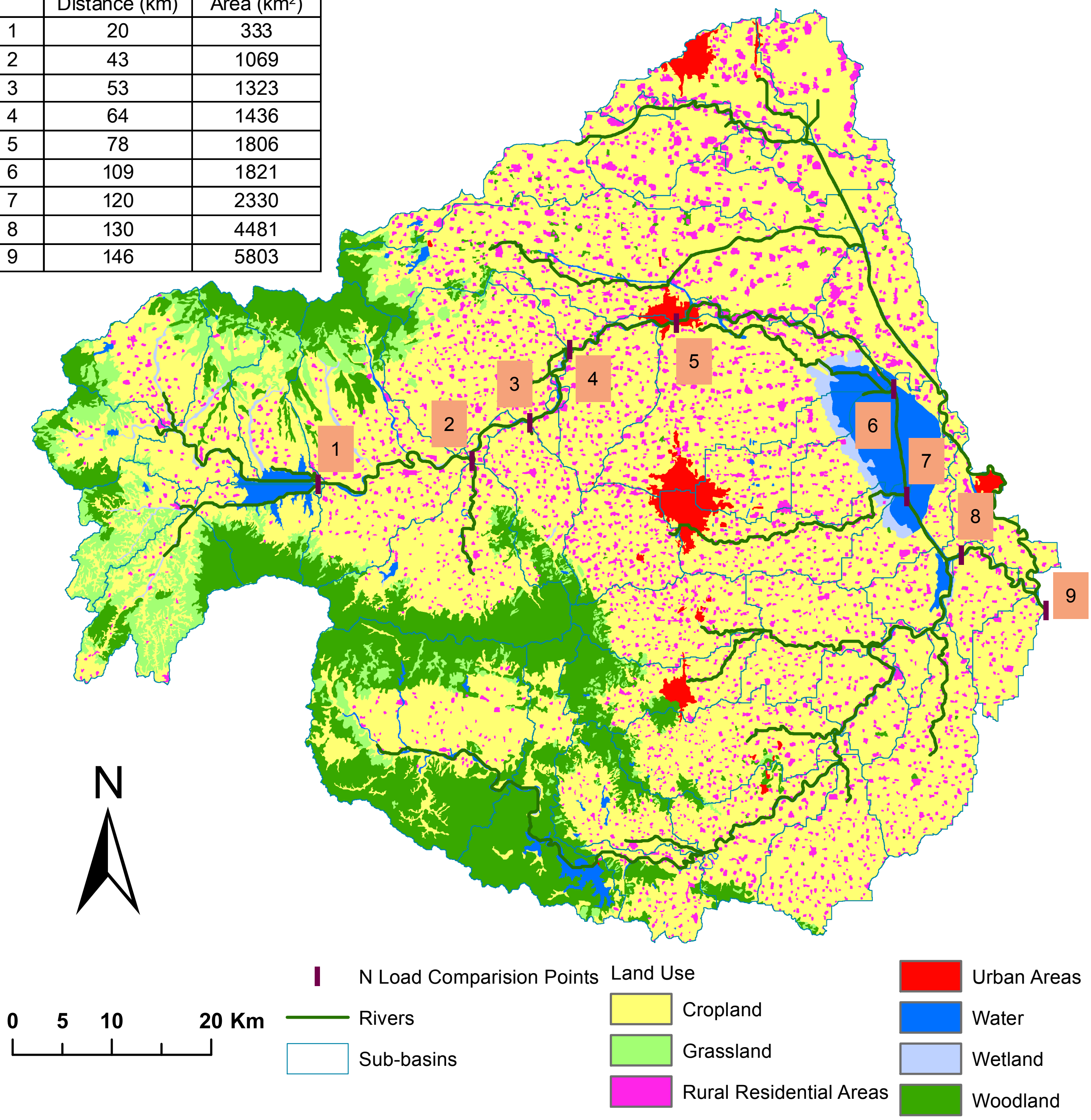


Fig. 3 - Locations of nine sub-basin outlets along the main reach of the Ru River for comparing TN and NH_4-N loads

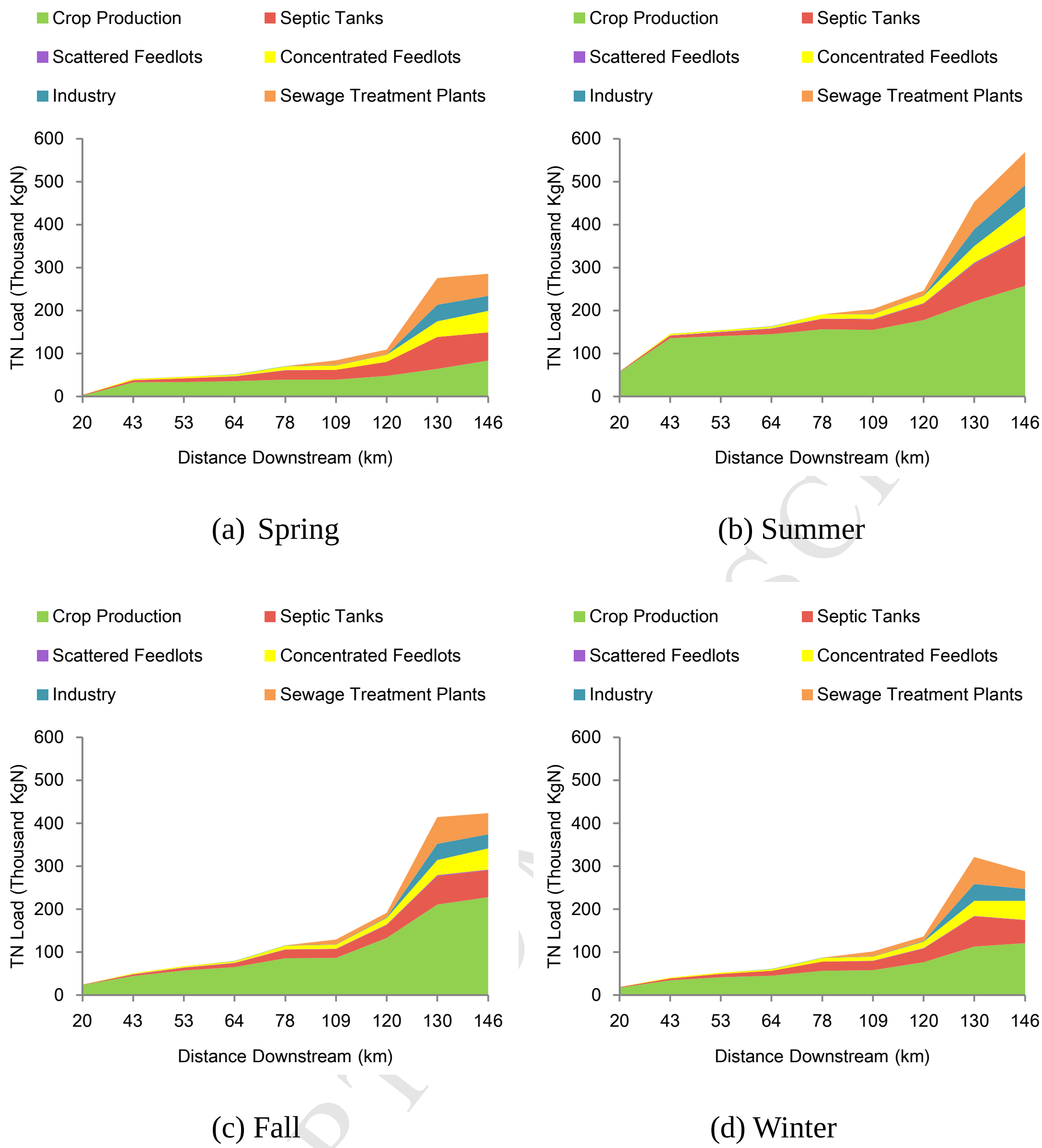


Fig. 4- Average monthly TN load from various pollution sources along the main reach of the Ru River in four seasons between 2006 and 2011: (a) Spring; (b) Summer; (c) Fall; and (d) Winter.

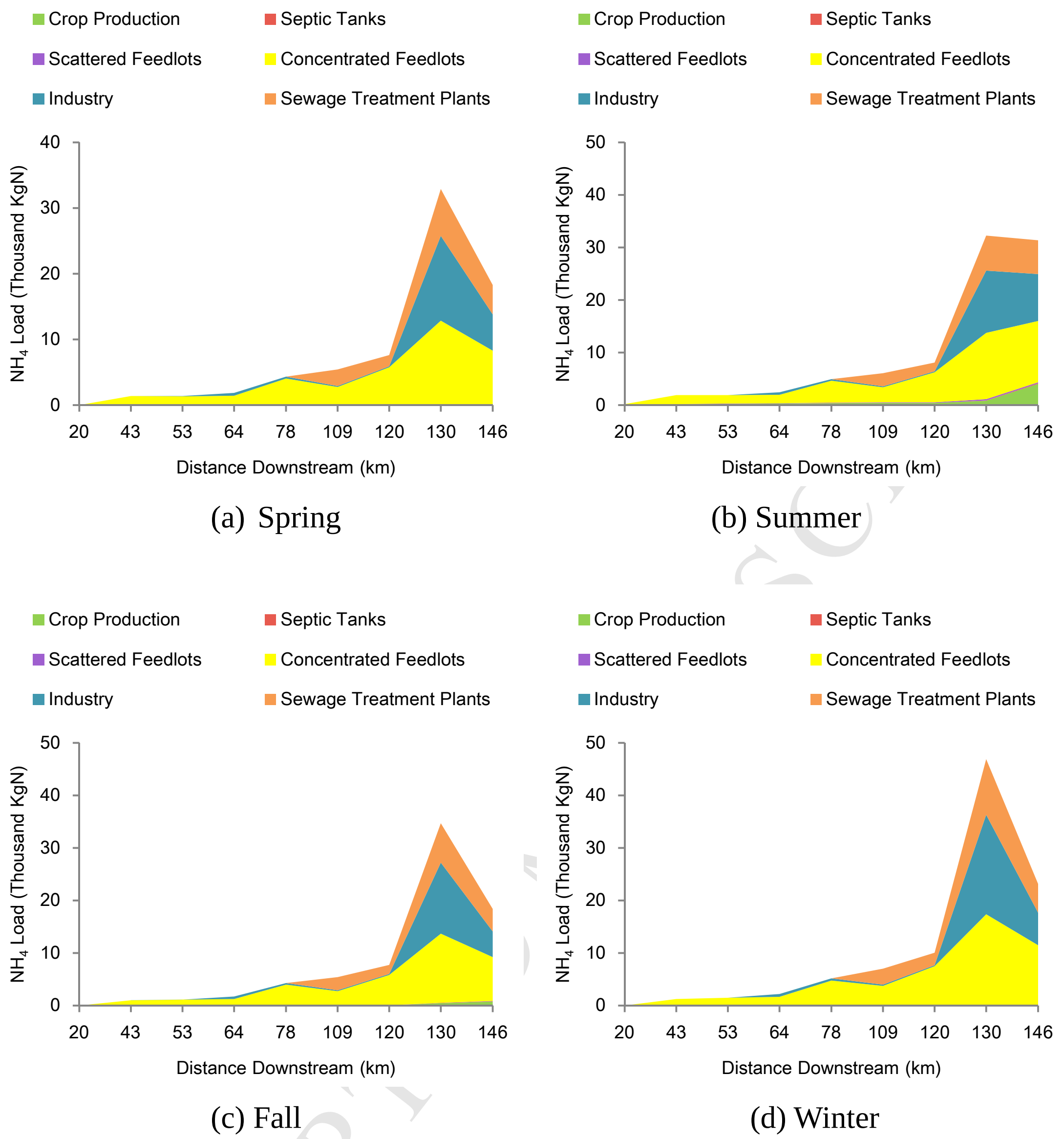
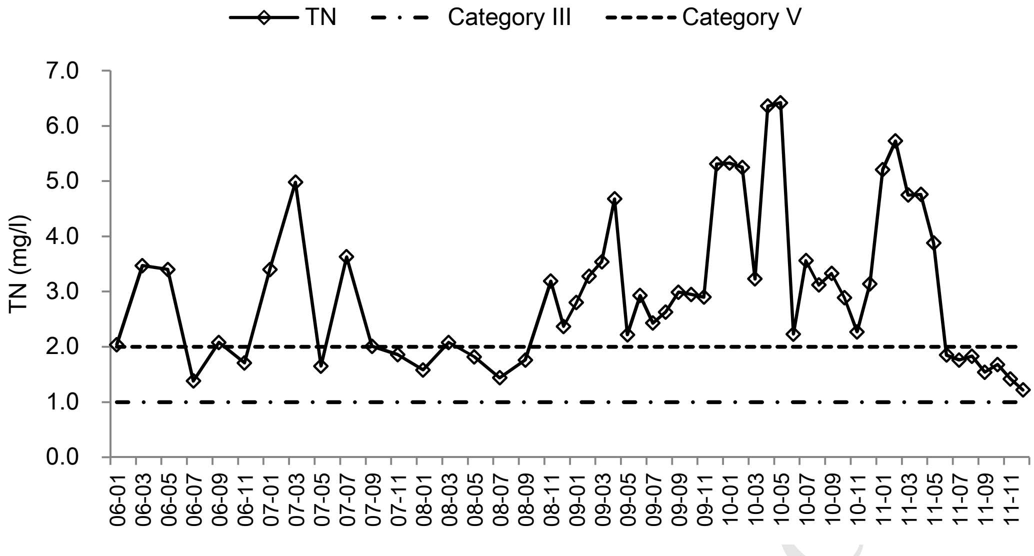
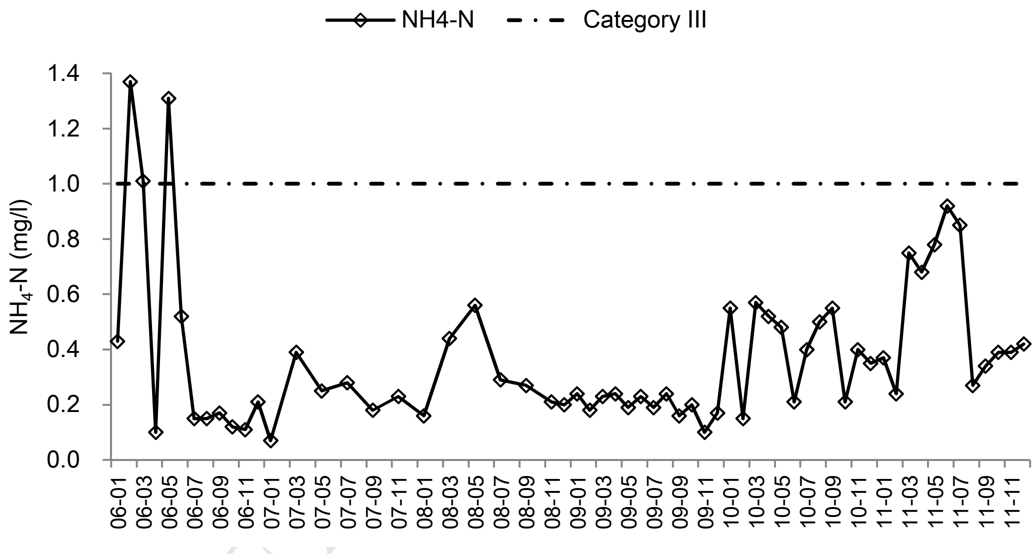


Fig. 5- Average monthly NH_4-N load from various pollution sources along the main reach of the Ru River in four seasons between 2006 and 2011: (a) Spring; (b) Summer; (c) Fall; and (d) Winter.



(a) TN



(b) NH_4-N

Fig. 6- Monthly TN and NH_4-N concentrations at the outlet of the Ru River Basin

Highlights

1) The SWAT models simulate N loads from all known anthropogenic pollution sources.
2) The SWAT models with daily and hourly rainfall are compared in N load simulation.
3) TN load from crop production is the largest followed by septic tanks in the basin.
4) NH_4-N load from concentrated feedlot operations is the largest in the basin.