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2 **Water and Nutrient Balances in a Large Tile-Drained**  
3 **Agricultural Catchment: A Distributed Modeling Study**  
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1 **Abstract**

2 This paper presents the development and implementation of a distributed model of coupled  
3 water nutrient processes, based on the representative elementary watershed (REW) approach,  
4 to the Upper Sangamon River Basin, a large, tile-drained agricultural basin located in central  
5 Illinois, mid-west of USA. Comparison of model predictions with the observed hydrological  
6 and biogeochemical data, as well as regional estimates from literature studies, shows that the  
7 model is capable of capturing the dynamics of water, sediment and nutrient cycles reasonably  
8 well. The model is then used as a tool to gain insights into the physical and chemical  
9 processes underlying the inter- and intra-annual variability of water and nutrient balances.  
10 Model predictions show that about 80% of annual runoff is contributed by tile drainage, while  
11 the remainder comes from surface runoff (mainly saturation excess flow) and subsurface  
12 runoff. It is also found that, at the annual scale nitrogen storage in the soil is depleted during  
13 wet years, and is supplemented during dry years. This carryover of nitrogen storage from dry  
14 year to wet year is mainly caused by the lateral loading of nitrate. Phosphorus storage, on the  
15 other hand, is not affected much by wet/dry conditions simply because the leaching of it is  
16 very minor compared to the other mechanisms taking phosphorous out of the basin, such as  
17 crop harvest. The analysis then turned to the movement of nitrate with runoff. Model results  
18 suggested that nitrate loading from hillslope into the channel is preferentially carried by tile  
19 drainage. Once in the stream it is then subject to in-stream denitrification, the significant  
20 spatio-temporal variability of which can be related to the variation of the hydrologic and  
21 hydraulic conditions across the river network.

22 **Key Words:** coupled modeling framework, tile drainage, process interaction

23

## 1 **1 Introduction**

2 Water, sediment, carbon and nutrient cycles occur over a multiplicity of time and space  
3 scales, and govern the dynamics and health of all ecosystems, which are of critical importance  
4 to the long-term sustainability of human habitation. Fluxes of water and the variability of  
5 water cycle dynamics are key drivers of coupled physical, biogeochemical, ecological and  
6 human systems. For example, soil moisture storage is a result of the water cycle processes of  
7 rainfall, storage, and movement, which are governed by climatic and landscape features. The  
8 amount of nitrate in the soil is a result of human additions at discrete times as well as  
9 continuous evolution of biogeochemical processes (transport and reaction), which depend on  
10 the magnitude and dynamics of water and carbon cycle processes. Likewise, sediment  
11 transport is governed by erosion, sedimentation and re-entrainment processes that are linked  
12 to water flow pathways and human activities. Biogeochemical processing and reprocessing  
13 occurs as the flow moves along a gradient in the intensity of land use, from urbanized and  
14 agricultural lands that are adjacent to a stream bank, through various levels of riparian  
15 vegetation and grassy waterways that separate streams from managed landscapes, and to well  
16 developed bottomland forest or areas of prairie grasses along tributary streams (David et al.,  
17 1997; Rhoads and Herricks, 1996).

18 The interactions and feedbacks between these subsystems that occur at all scales, however,  
19 are poorly understood, inadequately observed, and extremely complex. The gaps in our  
20 knowledge and understanding of these interacting processes limit our ability to make robust  
21 predictions and provide a solid basis for sustainable watershed management. Understanding  
22 the interactions between various water and biogeochemical processes is also important in the  
23 wider context of climate change and human induced land use and land cover changes, with  
24 suggestions that the hydrological cycle may be accelerating as a result. A coupled modeling

1 framework of these subsystems may open new opportunities for studying interacting  
2 hydrological and biogeochemical processes, contributing significantly towards improved  
3 predictive capability. The move towards such a coupled modeling framework is also  
4 motivated by the fact that many of the interacting natural processes cannot be observed  
5 directly – instead we are only able to observe spatial and temporal patterns of signatures  
6 arising from the process interactions. A pattern dynamical approach that is focused on the  
7 identification of internal process interactions on the basis of spatio-temporal patterns of  
8 outcomes is an emerging paradigm towards making robust predictions. Such an approach has  
9 to be facilitated by a combination of data mining and modeling analysis. The current  
10 modeling work is a first step in this direction.

11 The work on this paper has been especially motivated by the combination of biophysical (e.g.  
12 a plentiful supply of summer rains, and fertile, deep glacial till soils) and social factors (e.g.  
13 intensive agricultural advisory services, land use and conservation strategies, and advanced  
14 precision-agriculture technologies) that have made the U.S Mid-West the Nation's  
15 breadbasket, albeit with considerable local and remote environmental impacts, such as  
16 contributing to eutrophication problems in the Gulf of Mexico. Despite the importance of this  
17 region both in terms of agricultural productivity and as a contributor to the environmental  
18 problems faced by the Nation, there are still critical knowledge gaps about the complex  
19 interactions among the various interacting processes that contribute to local and regional  
20 water quality impacts.

21 The foundation of this coupled hydrological and biogeochemical process model is the  
22 distributed watershed model, THREW, based on the representative elementary watershed  
23 (REW) approach pioneered by Reggiani *et al.* (1998, 1999, 2000). In this study we have  
24 extended THREW to include the effects of tile drains, which is major human modification to

1 this agricultural landscape. Upon testing the water flow model, THREW is then extended  
2 further to include modules for the interactions between water flow processes and processes  
3 associated with the generation of both sediments and nutrients (N and P), which are taken  
4 from previously published work (Viney and Sivapalan, 1999; Viney *et al.*, 2000). The  
5 combined model is then applied to Upper Sangamon River Basin (USRB), a 3600 km<sup>2</sup> tile-  
6 drained agricultural catchment located in south-central Illinois, and calibrated on the basis of  
7 all available water quality data, including regional summaries. The model is then used to  
8 generate insights into the process interactions underlying the observed and model-generated  
9 spatio-temporal patterns.

10 The paper is organized as follows: Section 2 describes the distributed computational  
11 framework of coupled hydrological and biogeochemical processes at the catchment scale.  
12 Section 3 provides the background information on the case study area and data sources.  
13 Section 4 lays out the model application results for the water and nutrient modeling, followed  
14 by discussion on the hydrological and biogeochemical process interactions. Section 5 closes  
15 with the summary.

## 16 **2 Model Description**

### 17 **2.1 A spatially distributed hydrological model**

18 THREW is an existing distributed, physically-based hydrological model (Tian *et al.*, 2006;  
19 Tian *et al.*, 2008), and is built around the representative elementary watershed (REW)  
20 concept. Pioneered by Reggiani *et al.* (1998, 1999, 2000), the REW approach is essentially a  
21 thermodynamically consistent framework to derive balance equations directly at the meso-  
22 scale for distributed hydrological modeling. The REW in THREW is the smallest resolvable  
23 spatial unit of a meso-scale basin which has an explicit spatial boundary, and is the  
24 fundamental building block of the model. As shown in Figure 1, a river basin can be

1 descrittized into a specified number of REWs, which are linked to each other through the river  
2 network. Each REW comprises a pre-specified fixed number of sub-regions, which determine  
3 the organizational structure of the model, characterizing various hydrological processes and  
4 the accompanying exchanges of mass, momentum, energy etc. that occur within the REW.  
5 Although the REW has an explicit and invariant boundary, the boundaries between the sub-  
6 regions are mostly varying with time (Lee *et al.*, 2005, 2007; Tian 2006; Tian *et al.*, 2006). In  
7 the latest version of THREW the sub-regions are the saturated zone (s-zone), the unsaturated  
8 zone (u-zone), the vegetated zone (v-zone), the bare soil zone (b-zone), the snow covered  
9 zone (n-zone), the glacier covered zone (g-zone), the sub-stream network (t-zone), and the  
10 main channel reach (r-zone), as shown in Figure 1. To adequately capture the vertical  
11 movement of water and nutrient within soil column, the unsaturated zone is further divided  
12 into two layers, the upper unsaturated zone (u1-zone) and the lower unsaturated zone (u2-  
13 zone). The depth of u1-zone is usually fixed (for example, 0.3 m), and that of u2-zone is  
14 allowed to vary with the water table. The ensemble of REWs constituting the watershed also  
15 interact with each other by way of exchanges of mass, momentum and energy through the  
16 inlet and outlet sections of the associated channel reaches. The mass, energy and momentum  
17 balances within the individual zones within the REW, and between the REWs, are described  
18 using a coupled set of ordinary differential equations (ODE), derived from thermodynamic  
19 principles (mass conservation, Newton's laws of motion, 2<sup>nd</sup> Law of Thermodynamics) by  
20 averaging, with a minimum number of simplifying assumptions. These coupled set of  
21 ordinary differential equations, together with appropriate closure relations and geometric  
22 relations, are the equation set that lies at the heart of the numerical implementation of REW  
23 approach. They can be solved using an appropriate numerical algorithm, such as the CVODE  
24 solver (please refer to <http://www.llnl.gov/casc/sundials/>) currently adopted in the THREW  
25 model. Details of THREW, including the various (mass and force) balance equations, as well

1 as the details of the constitutive and closure relations, are not presented here for reasons of  
2 brevity. These are available in several previous publications (Tian *et al.*, 2006; Mou *et al.*,  
3 2008; Tian *et al.*, 2010).

#### 4 **Figure 1**

5 As a distributed hydrological model based on the REW approach, THREW model has  
6 significant advantages: 1) it is physically-based, distributed, and of moderate complexity, and  
7 thus computationally advantageous; 2) it has a modular framework, in that the various closure  
8 relations, i.e., parameterizations of exchange fluxes, can be altered without changing the  
9 overall structure and numerical features; 3) because the model formulation ultimately results  
10 in a set of balance equations relating to mass, momentum and energy stores (state variables),  
11 the coupled set of ODEs are already in state-space form and can be easily adapted for  
12 predictions and data assimilation purposes; and 4) compared to grid-based models, the REW-  
13 based distributed model will be more suitable for incorporating various types of land use  
14 zones, or water use zones, which are typically categorized by zones (urban areas, irrigation  
15 districts, etc.). Thus it will allow us to develop spatial connections between REW units (rather  
16 than grids) and water use zones. Moreover, THREW simulates the interactions between  
17 surface water, soil water and shallow groundwater (and if needed deep groundwater as well),  
18 which help facilitate inclusion of various types of nutrients; in turn this makes it possible to  
19 examine how and to what degree different components of the hydrologic cycle are interacting  
20 with different components of the biogeochemical cycles.

#### 21 **2.2 Extension to agricultural basins: tile drainage**

22 Although THREW has been applied to a number of basins in China, U.S. and Europe under  
23 various climate and landscape conditions, it has not been applied to an agricultural basin with  
24 extensive tile drains, as we have in the U.S. Mid-West. Field studies suggest that tile drainage,

1 where it exists, is usually a very important source of streamflow (Algoazany *et al.*, 2007;  
 2 Goswami, 2006). It is thus necessary to incorporate the process of tile drainage for successful  
 3 prediction in these agricultural basins.

4 Tile drainage is an artificial way to remove excess surface and subsurface water from the  
 5 water-logging land to enable crop growth (Ritzema, 1994). In the mid-west of U.S., tile drains  
 6 have been laid out under swamps and wetlands to deplete the soil water in the saturated zone,  
 7 and to maintain the water table to an acceptable level to facilitate agricultural production.  
 8 There have been numerous studies on tile drainage, and various modeling approaches have  
 9 been proposed such as the classical Hooghoudt equation (Hooghoudt, 1940), Kirkham  
 10 equation (Kirkham, 1958), Ernst equation (Ernst, 1956). Most of these drainage equations are  
 11 derived based on the Dupuit-Forchheimer assumptions. However, these equations require the  
 12 exact locations of the tile drains, which are not often available and, moreover, how their  
 13 effects up-scale to the watershed or REW scale is also not well quantified. Therefore, in this  
 14 paper we opt for a conceptual description of their drainage effects, in combination of REW-  
 15 scale effective parameters. In fact, the efficiency of tile drains is governed by the subsurface  
 16 water storage, i.e., the higher the water table is, the faster the saturated soil water is depleted  
 17 through the tile drains. It is thus not unreasonable to adopt a simple storage-discharge relation  
 18 to describe the integrated response of all tile drains present at the REW scale. In this work, we  
 19 adopt the following conceptual relationship to characterize drainage through tile drains at  
 20 REW scale:

$$21 \quad q_{tile} = \begin{cases} 0 & y_s \leq Z - z_{tile} \\ \alpha k_s [(y_s - (Z - z_{tile})) / z_{tile}]^\beta & y_s > Z - z_{tile} \end{cases} \quad (1)$$

22 where  $q_{tile}$  is the rate of saturated soil water being depleted to the channel through the tile  
 23 drains, [m/s], averaged through out the study area.  $k_s$  is the saturated hydraulic conductivity

1 which controls the subsurface flow into tile drains,  $[m/s]$ .  $Z$  is the total depth of soil column  
2 (from ground surface to an impervious layer),  $[m]$ .  $y_s$  is the depth of the saturated layer from  
3 the water table to the impervious layer,  $[m]$ .  $z_{tile}$  is the assumed depth of drainage tiles,  $[m]$ .  
4  $\alpha$  is a dimensionless constant which is mainly a function of the hydraulic properties of the  
5 tile drain network.  $\beta$  is an exponent parameter subject to the spatial layout of tile drain  
6 system. Equation 1 applies when the focus is on the integrated tile drainage response at large  
7 scale, and the detailed information about the tile drain system is not available or is  
8 incomplete.

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### 9 **2.3 Coupled model of water, sediment and nutrients**

10 The component models for suspended sediments, nitrogen and phosphorus are mostly taken  
11 from Viney and Sivapalan (1999) and Viney *et al.* (2000) with some minor modifications, and  
12 only brief summaries are presented here. Note that the processes governing suspended  
13 sediments, nitrogen and phosphorus are described at the sub-watershed scale, which makes  
14 them consistent with the scale at which hydrological processes are described within THREW.

15 As shown in Figure 2, the storages and exchange fluxes of sediments and nutrients are  
16 simulated for each of the sub-regions within a REW, and thus inevitably coupled to the water  
17 flow part. Direct interactions between the landscape and atmosphere (e.g., precipitation,  
18 fixation of nitrogen by plants, and the volatilization of ammonia) and between the basin and  
19 humans (e.g., fertilization and crop harvest) are associated with the v-zone and the b-zone.  
20 The vertical movement of nitrogen is coupled with the water movement in the unsaturated  
21 zone (u1-zone and u2-zone) and the saturated zone (s-zone). The lateral loading of sediments,  
22 phosphorus and nitrogen is triggered by surface and subsurface runoff generation and  
23 subsequent delivery to river reaches. For instance, the initiation (soil erosion) and routing of  
24 suspended sediments on hillslopes are driven by the generation and routing of surface runoff.

1 The fluxes of water and different substances are transported across the watershed through a  
2 set of REWs, which are organized around the river network (not shown in this figure).  
3 Presentations of more detailed process descriptions for phosphorus, nitrogen and suspended  
4 sediments that follow are adapted from Viney and Sivapalan (1999) and Viney *et al.* (2000).

### 5 **2.3.1 Sediment model**

6 The sediment model predicts surface erosion and the in-stream processes of deposition, bank  
7 and bed erosion, re-entrainment and settling. As in Viney and Sivapalan (1999), sediment  
8 generation is assumed to occur by upslope erosion processes associated with surface runoff  
9 and is based on a conceptualization of the Universal Soil Loss Equation (Wischmeier and  
10 Smith, 1978). Once in the stream, sediment transport processes are governed by a stream  
11 sediment capacity, which is controlled by the stream power. If a stream's predicted sediment  
12 load exceeds its carrying capacity, some sediment is deposited to the streambed and is  
13 available for subsequent re-entrainment. If the load is unable to satisfy capacity then sediment  
14 is re-entrained (subject to availability) or eroded from the stream-bank. Sediment in  
15 suspension within a REW is subject to a delivery ratio governed by the settling rate for  
16 sediment particles. The details of sediment process description are provided in Liu *et al.*  
17 (2009).

### 18 **2.3.2 Phosphorus model**

19 The phosphorus model describes the processes of precipitation, fertilization, plant uptake,  
20 residue decay, sorption, harvest losses, erosion, surface entrainment and subsurface discharge.  
21 Most of the phosphorus cycle models proposed in the literature (e.g., Neitsch *et al.*, 2005)  
22 separately consider the organic and inorganic stores, which are further subdivided into readily  
23 mobilized active pools and slowly changing less accessible stable pools. After Viney *et al.*  
24 (2000), we combine the organic and slowly changing and less accessible stable pools into one

1 single pool, and denote it as particulate phosphorus (PP). The readily-mobilized active pools  
2 have been combined into another single pool, denoted as dissolvable phosphorus (DP).  
3 Another pool of phosphorus is biological phosphorus. The key components of the phosphorus  
4 model are described below. For better understanding of these components and fluxes, Figure  
5 2 and Figure 6 could also be referred to, although the main purpose of Figure 6 is to show the  
6 mass balance of phosphorous and thus presented later.

#### 7 **(i) Phosphorus from rainfall**

8 Precipitation of inorganic phosphorus is assumed to occur at a specified concentration that,  
9 for simplicity, is assumed to be constant in time and space. As the surface runoff interacts  
10 with the underlying soil, it entrains an amount of soil inorganic phosphorus. The resulting  
11 entrained phosphorus augments the concentration of phosphorus already being carried by the  
12 surface flow.

#### 13 **(ii) Phosphorus from fertilizer**

14 The rate and timing of fertilizer application is determined by many factors, such as climate  
15 conditions, crop plantation, and soil properties and so on. The phosphorus from fertilizer,  
16 organic and inorganic, is assumed to contribute to the storage of the top soil layer.

#### 17 **(iii) Leaching of phosphorus**

18 Leaching of dissolvable phosphorus to deeper levels in the unsaturated zone and ultimately to  
19 the deep groundwater is neglected by the model because phosphorus anions are much more  
20 affiliated to soil particles rather than water molecules. While it is not doubted that phosphorus  
21 leaching can lead to significant groundwater pollution according to some standards, its effect  
22 on streamflow discharges is considered negligible since the primary sources of phosphorus  
23 discharge involve surface and near-surface processes.

1 (iv) Residue decay

2 The processes of leaf fall, crop residue accumulation and litter decay are captured by the  
3 single term “residue decay”. For a crop, a fixed proportion of the biomass phosphorus is  
4 assumed to contribute to residue decay after harvesting, and the rate is given by

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$$H_p = k_{HP} P_B \quad (2)$$

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6  $H_p$  should be regarded as a flux averaged throughout the study area, [kg/m<sup>2</sup>/s]. All the  
7 nutrient fluxes and storage items in the rest of this paper, unless specified, are averaged  
8 throughout the study area, and have the same units [kg/m<sup>2</sup>/s] or [kg/m<sup>2</sup>].  $k_{HP}$  is a constant  
9 coefficient, [1/s], which is non-zero during a certain period after harvesting, and zero during  
10 the remainder of time.  $P_B$  is biomass P accumulated during the growing period, [kg/m<sup>2</sup>]. For  
11 a forested field, the rate of residue decay is assumed to be the same as the rate of plant uptake.

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12 The rest of the biomass phosphorus is harvested and exported out, mainly in the form of grain.

13 (v) Plant uptake

14 Plant uptake rate of phosphorus is assumed to depend on the rate of canopy biomass  
15 accumulation and therefore varies seasonally. This uptake is extracted from the dissolvable  
16 (i.e., labile) phosphorus stores provided that there is sufficient supply, and the rate is given by

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17 
$$U_p = k_{UP} \frac{dLAI}{dt} \quad (3)$$

18 Plant uptake transfers soluble inorganic P to biomass P. In Equation (3),  $k_{UP}$  is a constant

19 coefficient, [kg/m<sup>2</sup>].  $\frac{dLAI}{dt}$  is the rate of increase of leaf area index (LAI), [1/s], and it is

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20 assumed that there is no P uptake when LAI decreases or dissolvable phosphorus storage is  
21 completely depleted.

1 **(vi) Mineralization/immobilization and desorption/adsorption**

2 Fluxing between the dissolvable and organic forms is typically achieved through the  
3 complementary processes of mineralization and immobilization, while fluxing between the  
4 dissolvable and adsorbed forms is through the processes of desorption and adsorption. Since  
5 the organic and adsorbed pools have been combined into a single pool, which we expect to be  
6 dominated by the organic component, we could model the net desorption/mineralization flux  
7 in term of a simple desorption equation

8 
$$M_P = k_{MP} \frac{1}{1+r} (P_O - rP_I) \quad (4)$$

9 where  $k_{MP}$  is a constant coefficient,  $[1/s]$ ,  $P_O$  is the storage of organic phosphorus,  $[kg/m^2]$ ,  
10  $P_I$  is the storage of inorganic phosphorus,  $[kg/m^2]$ ,  $r$  is phosphorus retention index,  $[-]$ ,  
11 which is a function of soil type, but in this work a universal value is applied to all soil types  
12 for simplicity. It is also assumed that this fluxing does not occur if the soil temperature is  
13 below zero degree Celsius (Neitsch *et al.*, 2005, p190). Note the net desorption/mineralization  
14 flux (from the organic phosphorous store) contributes to the inorganic phosphorus store, while  
15 the residue decay (from the biomass phosphorous store) contributes to the organic  
16 phosphorous store.

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17 **(vii) Phosphorus movement with water flux**

18 Due to its low mobility, soluble phosphorus only moves with surface water flux, including  
19 infiltration excess runoff and saturation excess runoff, and the lateral loading rate of DP from  
20 hillslope into channel is therefore given by

21 
$$S_P = k_{SP} q_s P_I \quad (5)$$

1 where  $k_{sp}$  is a constant coefficient, [1/m], and  $q_s$  is the lateral water discharge rate (averaged  
2 throughout the study area) from hillslope into the channel, [m/s]. During the transportation of  
3 DP through the river network there is no mineralization/immobilization or  
4 desorption/adsorption in the channel flow.

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#### 5 (viii) Phosphorus movement with sediment flux

6 Upslope erosion of organic and adsorbed phosphorus occurs in conjunction with surface  
7 sediment erosion and is dependent on the occurrence and presence of surface runoff. Eroded  
8 phosphorus is preferentially attached to the finer sediment particles, which in turn tend to be  
9 the first eroded. Consequently, the concentration of eroded phosphorus decreases as the mass  
10 of eroded material increases. In the absence of quantitative information on the concentration  
11 of organic and adsorbed phosphorus in the upper layers, the model assumes an enrichment  
12 ratio for upslope erosion as a function of the amount of sediment erosion. The transport of  
13 attached nutrients with channel flow is not conservative since the exchange of suspended  
14 sediment and channel floor is incorporated.

### 15 2.3.3 Nitrogen modeling

16 The nitrogen model has a similar structure to that of phosphorus. The nitrogen fluxes for plant  
17 uptake, harvest/residue decay, surface entrainment and the mobilization and transport of  
18 particulate nitrogen are modeled analogously to the corresponding phosphorus fluxes, and  
19 will not be repeated here (for more details see Viney et al., 2000). The nitrogen modeling,  
20 nonetheless, is more complex for a few reasons. One is the need to separately predict  $\text{NO}_3\text{-N}$   
21 and ammonium forms of the dissolvable inorganic component, which necessitates the  
22 inclusion of an extra flux, nitrification, to account for nitrogen cycling between these two  
23 forms. Secondly, unlike phosphorus, nitrogen undergoes gaseous exchange with the  
24 atmosphere, and this exchange has to be modeled explicitly through the processes of

1 ammonium volatilization, denitrification and nitrogen fixation. Furthermore, as  $\text{NO}_3\text{-N}$  is  
2 highly dissolvable, its leaching to deeper levels in the soil profile is a significant loss  
3 mechanism, and an explicit modeling of that process is included. For better understanding of  
4 these components and fluxes, Figure 2 and 7 could also be referred, although the main  
5 purpose of Figure 7 is to present the mass balance of nitrogen.

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#### 6 **(i) Atmospheric N fixation**

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7 Plant fixation converts atmospheric N (mainly  $\text{N}_2$ ) into ammonia, which is directly utilized by  
8 numerous prokaryotes in the soil. Therefore it delivers nitrogen from the atmosphere to the  
9 ammonium pool. not to the biomass nitrogen store. The plant fixation rate is modeled as a  
10 function of vegetation status.

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$$11 \quad F_N = k_{FN} LAI \quad (6)$$

12  $k_{FN}$  is a constant coefficient,  $[\text{kg}/\text{m}^2/\text{s}]$ .

#### 13 **(ii) Nitrification and volatilization**

14 Nitrification transfers ammonium to nitrate when the soil temperature is higher than a certain  
15 value, and the rate is given by

$$16 \quad J_N = k_{JN} N_{NH4} \quad (7)$$

17  $k_{JN}$  is a constant coefficient,  $[1/\text{s}]$ .  $N_{NH4}$  is ammonium storage in the soil,  $[\text{kg}/\text{m}^2]$ .

18 Volatilization releases a fraction of ammonium storage as ammonia gas into the atmosphere  
19 and is also simulated as a fixed proportion of the ammonium nitrogen pool when the soil  
20 temperature is higher than a certain value.

#### 21 **(iii) Field denitrification**

1 The hillslope denitrification process is microbially mediated and occurs primarily in anoxic  
 2 conditions. In the model, this process is assumed to occur as a fixed proportion of the NO<sub>3</sub>-N  
 3 pool and occurs only if the soil water content is greater than 90% of the saturated soil  
 4 moisture content and the soil temperature is higher than a certain value (Williams *et al.*, 1984;  
 5 Neitsch *et al.*, 2005).

$$6 \quad G_N = \begin{cases} k_{GN} N_{NO3} & \theta / \theta_s > \theta_c / \theta_s \\ 0 & \theta / \theta_s \leq \theta_c / \theta_s \end{cases} \quad (8)$$

7  $k_{GN}$  is a constant coefficient,  $[1/s]$ .  $N_{NO3}$  is the storage of NO<sub>3</sub>-N in the soil,  $[kg/m^2]$ .  $\theta$  is  
 8 the soil moisture content.  $\theta_s$  is the saturated soil moisture content.  $\theta_c$  is a threshold soil  
 9 moisture content. Here  $\theta_c / \theta_s$  is taken as 0.9 after Williams *et al.* (1984).

#### 10 (iv) Nitrogen movement and variation within soil column

11 Ammonium is easily attracted by negative-charged soil particles, while nitrate is highly  
 12 mobile. Therefore it is assumed that all nitrate storage is soluble and movable with water. The  
 13 nitrate storage in the unsaturated soil layer will lose nitrate due to denitrification, plant uptake  
 14 and leaching, and receive nitrate due to infiltration, nitrification and fertilization. The nitrate  
 15 storage in saturated soil layer only exchange nitrate with other zones by the way of water flux.

#### 16 (v) Nitrogen movement with water flux

17 Nitrate is highly soluble and moves with all types of water fluxes, including infiltration excess  
 18 runoff, saturation excess runoff and subsurface flow (or tile drainage). The lateral loading of  
 19 nitrate is simulated similar to that of DP. The transportation of nitrate through the river  
 20 network is not conservative, i.e., in-stream denitrification is considered.

#### 21 (vi) In-stream denitrification

1 While traveling through the river network, NO<sub>3</sub>-N is removed due to in-stream denitrification  
2 process. After Donner *et al.* (2004) and Wollheim *et al.* (2006), the instantaneous fractional  
3 removal ratio is defined as

$$4 \quad Rr = \frac{v_f}{H_L} \quad (9)$$

5 where  $v_f$  is the apparent nutrient uptake velocity [m/s],  $H_L$  is the hydraulic load [m/s]. In the  
6 THREW model,  $H_L$  is estimated as

$$7 \quad H_L = \frac{h}{\tau} \quad (10)$$

8 where  $h$  is the water depth [m],  $\tau$  is the mean residence time [s] given by

$$9 \quad \tau = \frac{l}{v} \quad (11)$$

10  $l$  is the reach length [m],  $v$  is the water velocity [m/s]. Note that  $\tau$  is essentially the mean  
11 travel time of NO<sub>3</sub>-N through the main channel zone (r-zone) within each REW. NO<sub>3</sub>-N joins  
12 the main channel from mainly two sources: the inflow from upstream channel and lateral  
13 loading from the hillslope. For the NO<sub>3</sub>-N from lateral loading, the mean in-channel travel  
14 time is in fact about half of that of the NO<sub>3</sub>-N from upstream inflow. But here it is assumed  
15 that the major part of the in-stream NO<sub>3</sub>-N comes from the upstream inflow. This assumption  
16 is appropriate for large basins.

#### 17 **(vii) Nitrogen movement with sediment flux**

18 The movement of organic and adsorbed nitrogen with suspended sediment is simulated  
19 similarly to PP.

### 1 3 Study area and data

2 The present modeling study was carried out on the Upper Sangamon River Basin (USRB) in  
3 central Illinois, which is representative of the processes and problems associated with  
4 agricultural landscapes in the Mid-West region. USRB, with a drainage area of 3,600km<sup>2</sup>, is  
5 an agricultural basin with intensive row-crop production. Soil in this basin is dominated by  
6 poorly drained silt clay loams and silt loams, and very fertile due to high organic content  
7 (Demissie and Keefer, 1996). The topography is very flat, with the average slope of the main  
8 channel as 0.00049. According to Demissie and Keefer (1996), in 1994, row crops (corn and  
9 soybean) covered 85.3 percent of the whole basin area and grassy crops (small grains and  
10 hay) covered 2.4 percent. Corn and soybean almost equally share the row crop land area. The  
11 percentage of area covered by corn is 42.0, and by soybean is 43.3 percent, respectively. The  
12 biogeochemistry of USRB is altered annually in the spring and fall with widespread yet  
13 highly variable applications of nitrogen and phosphorus fertilizers. Current land and  
14 watershed management practices, such as dredging of channels, produce rapid transmission of  
15 nitrogen and phosphorus from the land surface through soils, riparian areas, and small streams  
16 to larger streams and rivers. The extensive production of corn and soybeans, substantial inputs  
17 of urban wastewater and agricultural runoff, and modification of the drainage network have  
18 altered patterns and rates of nitrogen and phosphorus cycling.

### 19 Figure 3

20 The Illinois State Water Survey (ISWS) has conducted a watershed monitoring project for the  
21 Lake Decatur watershed, which is a part of USRB (Keefer and Bauer, 2008). They have  
22 measured streamflows, and sediment and nutrient concentration at several stations, including  
23 Big Ditch and Monticello. As shown in Figure 3, downstream of Monticello is Lake Decatur  
24 which has a significant impact on the movement of water and transport of sediments and

1 nutrients. For the sake of simplicity, in this work we only focus on the drainage area upstream  
2 of Monticello. In order to examine the spatial variability of water and biogeochemical  
3 processes, observations at two locations along the Upper Sangamon River with distinct  
4 drainage areas have been chosen for this study, namely Big Ditch and Monticello. The  
5 upstream drainage area of Big Ditch is about 134.2km<sup>2</sup> and of Monticello is about 1379.8  
6 km<sup>2</sup>.

7 ~~DEM data with 30m resolution from the USGS National Elevation Dataset was used to~~  
8 ~~delineate the geometric information, including sub-catchments which are the building blocks~~  
9 ~~of the THREW model linked by the channel network.~~ Hourly observations of precipitation  
10 ~~were from National Climate Data Center (NCDC) of National Oceanic and Atmospheric~~  
11 ~~Administration (NOAA). Hourly stream discharge, irregularly sampled concentration values~~

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12 of suspended sediments, NO<sub>3</sub>-N, and dissolved phosphorus were obtained from the long term  
13 monitoring project by ISWS (Keefer and Bauer, 2008). Hourly soil temperature data were  
14 obtained from the Water and Atmosphere Resources Monitoring Program conducted by  
15 ISWS. Potential evaporation time series were extracted from the NOAA/NARR dataset.  
16 Vegetation data including LAI were downloaded and extracted from MODIS/terra dataset.  
17 Soil properties such as porosity and saturated hydraulic conductivity were extracted from the  
18 STATSGO database. The study period is from 10/01/1993 to 09/30/2004, and was chosen  
19 according to data availability.

20 The application of nitrogen and phosphorus fertilizers is an important external input to the  
21 catchment, which often exhibits high spatial and temporal variability. Empirical values of  
22 fertilization have been obtained from literature and through personal communication  
23 (McIsaac & Hu, 2004; McIsaac, G., personal communication). For the sake of simplicity, the  
24 application of fertilizers is assumed to be spatially uniform and to be carried out twice a year,

1 the first one during March 15-April 1, and the next during November 1-November 15 (Hu *et*  
2 *al.*, 2007). In most of the areas corn and soybean are planted in rotation. We assume for  
3 simplicity that, in each year, 50% of the field area is corn and another 50% is soybean. The  
4 harvest of both corn and soybean is assumed to occur in mid-September.

## 5 **4 Results and discussion**

### 6 **4.1 Model application**

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7 As shown in Figure 3, for the implementation of the coupled model, the whole USBR area has  
8 been divided into 51 REWs (3600km<sup>2</sup>). In this work, nonetheless, the analysis is only focused  
9 on the area upstream of Monticello station (1400km<sup>2</sup>), which consists of 19 REWs. The  
10 coupled model has been run using an hourly time step. The objective is to characterize water  
11 and nutrient balances and their process controls, and to gain an understanding of the  
12 interactions between hydrological and biogeochemical processes in agricultural landscapes in  
13 the U.S. Mid-West.

14 We divide the whole study period into two parts: a warm-up period, 10/01/1993~09/30/1994,  
15 and a calibration period, 10/01/1994~09/30/2004. We use multiple criteria for calibration. For  
16 the water part the criteria include optimal Nash-Sutcliffe coefficient ([Nash and Sutcliffe,](#)  
17 [1970](#)) and the percent bias (defined as the ratio of the difference between simulated and  
18 observed runoff volume to the observed runoff volume, Ivanov *et al.*, 2004). Some other  
19 signatures of temporal variability are also used during the calibration, such as the regime  
20 curve and the flow duration curve, in order to improve the fit of model predictions to  
21 observations. For suspended sediments, nitrogen and phosphorus, the calibration has been  
22 conducted in order to: a) satisfy regional mass balances indicated by the empirical data  
23 presented in the literature; b) match the predicted time series to the observed time series as  
24 well as possible.

1 **Figure 4**

2 Figure 4 shows simulated and observed streamflow at Monticello station at both the hourly  
3 and seasonal scale (i.e., mean monthly streamflows). The results show strong seasonality with  
4 two peaks (during winter and spring) and low flows during summer and fall. Comparison  
5 between the observed and predicted hydrographs and regime curves suggests that the model  
6 captures the variation of streamflow very well at both the hourly and seasonal scale. For the  
7 period of 10/01/1994~09/30/2004, the Nash-Sutcliffe efficiency on the basis of hourly flows  
8 is 0.67, and the percent bias is 0.05.

9 **Figure 5**

10 Figure 5 shows the model predicted time series of  $\text{NO}_3\text{-N}$  concentrations and dissolved  
11 phosphate concentrations (at hourly time step) and the observed time series (at irregular time  
12 intervals). We are not presenting the results for suspended sediments, due to lack of data to  
13 fine tune model, calibrate model parameters and validate model predictions. The temporal  
14 variation of  $\text{NO}_3\text{-N}$  concentration has been well captured by the model at both Big Ditch and  
15 Monticello. It can be inferred that the  $\text{NO}_3\text{-N}$  loads (product of water discharge and  $\text{NO}_3\text{-N}$   
16 concentration) has also been satisfactorily reproduced. On top of this, one might notice that  
17 the  $\text{NO}_3\text{-N}$  concentration at Monticello appears to be lower than that at Big Ditch. This  
18 decrease of  $\text{NO}_3\text{-N}$  concentration from upstream to downstream may most likely be due to in-  
19 stream denitrification process, which will be discussed later. As for dissolved phosphorus, the  
20 model captures the temporal variation at Big Ditch, but significantly underestimates the  
21 concentration of dissolved phosphorus at Monticello, especially in the summer and fall  
22 seasons. A possible explanation for this under-estimation is the effluent discharge from the  
23 urban areas between Big Ditch and Monticello, including the towns of Mahomet and  
24 Monticello. Effluent from the local sewer system and wastewater treatment plants is

1 discharged into the Sangamon River, which introduces non-negligible amounts of nutrients  
2 into the river, especially phosphorus. Dissolved phosphorus from effluent discharge, in the  
3 form of point-source pollution could make a significant contribution to the in-stream  
4 concentrations of phosphorus in the summer and fall seasons. The amount of nitrogen such as  
5 nitrate from effluent discharge is rather small comparing to the other sources contributing to  
6 the channel, so its impacts on the nitrate concentration is insignificant. Nevertheless, nutrients  
7 inputs through effluent discharges are not included in the current version of the model

8 **Figure 6**

9 **Figure 7**

10 As mentioned before, model calibration involved not only comparisons of model predicted  
11 against observed time series within the USRB, but also checks of broad measures of water  
12 and nutrient balances (regional space scale and annual time scale) against published estimates  
13 from Illinois region, to ensure that model predictions are consistent. Tables 1 and 2 present a  
14 comparison of various aspects of regional nitrogen and phosphorus balances between model  
15 predictions within USRB and regional estimates obtained from the literature (McIsaac and  
16 Hu, 2004; Hu *et al.*, 2007; David and Gentry, 2000; Howarth *et al.*, 1996; Gentry *et al.*,  
17 2009), demonstrating reasonable consistency in both N and P predictions.

18 Upon completion of model calibration (as in the above), model simulations were performed to  
19 generate an annual average and catchment-wide picture of the fate of both nitrogen and  
20 phosphorus. The results are presented in Figure 6 (for phosphorus) and Figure 7 (for  
21 nitrogen). In the case of P, the main input is fertilizer (30 kg. P/ha/yr) and the main output is  
22 annual harvest (of the crops) which takes out almost 29.6 kg. P/ha/yr, with relatively small  
23 amounts exported to rivers in dissolved form (0.3 kg. P/ha/yr) and in particulate form (0.5 kg.  
24 P/ha/yr). There is of course considerable internal processing (plant uptake, generation of plant

1 residue and mineralization), which are included in the model in conceptual form (see Viney *et*  
2 *al.*, 2000 for details). The picture is very different and more complex in the case of N, where  
3 in addition to fertilizer application (95 kg. N/ha/yr) in the form of ammonia, there is in  
4 addition large amount of fixation by plants (65 kg. N/ha/yr), and small amount of  
5 precipitation (10 kg. N/ha/yr). The resulting total inputs (170 kg. N/ha/yr) is partitioned into  
6 removal through harvest (116 kg. N/ha/yr), release into atmosphere in gaseous form (16 kg.  
7 N/ha/yr), and the removal through runoff in dissolved form (32 kg. N/ha/yr) and particulate  
8 form (5 kg. N/ha/yr). The biggest component (more than 90%) of the runoff export is through  
9 tile drainage. Just as in the case of P, there is considerable internal processing, including the  
10 conversion of organic nitrogen (as in plant residue) to ammonia through mineralization, from  
11 ammonia to nitrate through nitrification and from nitrate into nitrogen through denitrification,  
12 as well as plant uptake and generation of plant residue. These processes are of course included  
13 in the model in conceptual form (see Viney *et al.* 2000 for details). Knowledge of these  
14 relative estimates is extremely useful for targeting future research towards understanding and  
15 quantifying key components of the annual nutrient balances, and associated process controls.

#### 16 **4.2 Multi-scale interactions between water and nutrient cycling processes**

17 In spite of the average water and nutrient balances presented in Figures 6 and 7, there is  
18 considerable temporal (and spatial) variability in the nutrient mass balances, which are  
19 intimately related to climatic and hence hydrological variability at multiple time scales. The  
20 coupled model predictions are next used to throw light on these interactions, and the resulting  
21 temporal patterns.

#### 22 **Figure 8**

23 Figure 8 shows the relationship between the annual runoff and annual mass balance of  
24 nitrogen and phosphorus at the basin scale. Annual runoff depth is a hydrological indicator

1 and is itself a result of the interactions between variability in climatic forcing and landscape  
2 properties. Roughly, the wetter the climate (due to more precipitation or less evaporative  
3 energy) is, the larger the annual runoff depth. Therefore the annual runoff depth can be  
4 regarded as a a first order indicator of the inter-annual variability of wet/dry conditions,  
5 recognizing that some of the inter-annual variability of runoff could be caused by variability  
6 in intra-annual variability of climate forcing. In Figure 8, annual balance of nitrogen and  
7 phosphorus is expressed in terms of total annual mass brought into the basin, total annual  
8 mass exported out of the basin, and annual storage change within the basin. The results  
9 presented in Figure 8 show that total nitrogen inputs, dominated by fertilizer and plant  
10 fixation, do not show a significant relationship with annual runoff. Although annual  
11 precipitation clearly impacts annual runoff, the concentration of nitrogen in the precipitation  
12 is small, so the annual mass of deposition through precipitation is negligible compared to the  
13 corresponding amounts of fertilizer application and plant fixation. Fertilizer application is  
14 human related, and is assumed constant in this study. Plant fixation is a function of nutrient  
15 storage and the growing status of the crops, and does lead to significant inter-annual  
16 variability of the annual nitrogen inputs. But this inter-annual variability of nitrogen inputs is  
17 much less than that of nitrogen outputs, and for environmental reasons, our focus is thus on  
18 the latter. Total nitrogen output, including river loading (export) of nitrogen, field  
19 denitrification and volatilization, in-stream denitrification and grain export (through harvest),  
20 show an increasing trend with annual runoff depth. Correspondingly, this contributes to a  
21 systematic decrease of nitrogen storage with increase of annual runoff depth, from a positive  
22 change (storage supplement) during dry years to a negative change (storage depletion) during  
23 wet years. Inter-annual variability of phosphorous mass balance, on the other hand, is similar  
24 to that of nitrogen, but the variations of the output, and thus the storage, are much smaller

1 compared with the magnitude of annual phosphorous input (i.e., compare the units of the  
2 vertical axes in Figure 8).

### 3 **Figure 9**

4 In order to gain more insights into predicted behavior between the annual nitrogen output and  
5 annual runoff depth, and the mediating role of nitrogen storage/depletion, the annual  
6 variations of various components of the nitrogen output are plotted against annual runoff  
7 depth, as shown in Figure 9. Firstly, the results show that in the case of both N and P, grain  
8 export is the largest component of the annual export (as was already pointed out in Figures 6  
9 and 7). The model results in Figure 9 show that in the case of N, grain export is slightly  
10 decreasing with annual runoff, whereas non-grain export increases significantly with annual  
11 runoff. In the case of P the changes with annual runoff depth are quite small and negligible.  
12 Note that grain export is a significant portion of annual accumulated biomass gain (from plant  
13 uptake), and plant uptake itself is subject to many factors such as soil moisture, soil  
14 temperature, crop growing status and nitrogen storage in the soil.

15 The bottom panel of Figure 9 presents the breakdown of the non-grain part of the nutrient  
16 export into its various components. In the case of N, the biggest component is riverine  
17 dissolved export, which increases strongly with increase of annual runoff. The other three  
18 major components, i.e., field denitrification & volatilization, riverine denitrification and  
19 particulate riverine export are smaller, relative to the riverine dissolved export, but also appear  
20 not to be dependent on annual runoff. One can therefore see the connection between the  
21 increased dissolved nitrate export and depletion of nitrate storage during wet years, and  
22 decreased nitrate export and accumulation of nitrate storage in dry years. The net result of this  
23 is that average annual concentrations of dissolved nitrate in rivers in this region can remain  
24 constant between years, a type of *chemostatic behavior* that is being widely reported (Darracq

1 *et al.*, 2008; Godsey *et al.*, 2009; Basu *et al.*, 2010). On the other hand, while the results for P  
2 show a strong dependence on annual runoff, the magnitudes are so low that one cannot draw  
3 definitive conclusions.

#### 4 **Figure 10**

5 The interaction between hydrological and biochemical processes is manifested not only in the  
6 inter-annual variability, but also in the intra-annual variability. For example, Figure 10 shows  
7 the monthly variation of nitrogen storage and streamflow. Nitrogen storage variation is  
8 subject to both the input and output. The input components of nitrogen include: a) fertilizer,  
9 which is applied twice a year, in March and November; b) plant fixation, which is a function  
10 of crop growth status and peaks in July and August when the crop is flourishing most; and c)  
11 precipitation deposition (which is minor). The output components of nitrogen consist of: a)  
12 grain export which is assumed to occur once a year in late Fall; b) nitrate load through river  
13 network, which peaks in May and June; c) field denitrification and volatilization which  
14 mainly occur during the non-winter period when the temperature is above a certain threshold;  
15 d) in-stream denitrification and particulate nitrogen load (which are minor). From Figure 10  
16 one can see that the nitrogen storage peaks twice a year due to fertilizer application, and is  
17 depleted significantly in the month of September due to harvesting and during winter and  
18 spring when the highest amount runoff is produced. Among the output components,  
19 harvesting and riverine export are relatively significant and play an important role in the  
20 depletion of nitrogen storage. For phosphorus, the inputs are dominated by fertilizer  
21 application, and the outputs are almost completely dominated by grain export. Riverine export  
22 of DP and PP do not appear to have any significant impact on phosphorus storage variations.

#### 23 **Figure 11**

1 Further insights into the role of the interactions between hydrological and biochemical  
2 processes on nutrient export, as shown in Figures 9 and 10, can be gained by exploring the  
3 relative effects or contributions of different runoff generation components. Figure 11 shows  
4 the breakdown of three components of runoff generation within USRB watershed, and the  
5 fractions of NO<sub>3</sub>-N lateral loading (from the hillslope into the channel) carried by these  
6 different runoff components. Figure 11a shows that tile drainage is the most important runoff  
7 component right through the year, and takes up about 80% of the annual runoff generated  
8 within USRB. This is consistent with the field observations in neighboring regions with  
9 similarly intensive tile drain systems and similar soils and topography (Algoazany *et al.*,  
10 2007; Goswami, 2006). Dunne (saturation excess) overland flow and subsurface stormflow in  
11 the catchment constitute relatively small fractions of total runoff, whereas Hortonian runoff  
12 (infiltration excess) is virtually negligible. Figure 11b shows the corresponding breakdown of  
13 the total nitrate export into components carried by the three different runoff generation  
14 mechanisms. The results show that tile drains carry even a larger fraction of the nitrate  
15 removed in dissolved form by runoff. Particulate nitrogen is mainly carried by surface runoff,  
16 along with the sediment flux.

17 **Figure 12**

18 Once the nutrients are delivered to the nearest river reach, they are then transported down the  
19 stream network. Figure 12 shows the riverine export of nitrogen, showing the dissolved  
20 component is the dominant component, whereas riverine export of particulate nitrogen (the  
21 part carried by the suspended sediment) is rather small, since it is carried mainly by the  
22 Dunne overland flow (which is small). Note that the seasonal variation of riverine export of  
23 NO<sub>3</sub>-N is in phase with the seasonality of streamflow (especially tile drain flows).

24 **Figure 13**

1 The riverine flux of NO<sub>3</sub>-N, before being exported out of the basin, is subject to in-stream  
2 denitrification, which is usually considered a significant loss (Alexander *et al.*, 2009; David &  
3 Gentry, 2000; Howarth *et al.*, 1996). In USRB, the obvious decrease of NO<sub>3</sub>-N concentration  
4 from Big Ditch (upstream) to Monticello (downstream), as shown in Figure 5, is an indicator  
5 of this process. Our model study shows that, without incorporation of in-stream denitrification  
6 process this decrease of NO<sub>3</sub>-N from upstream to downstream cannot be reproduced. The rate  
7 of in-stream denitrification is controlled by many hydrological and biogeochemical factors,  
8 such as channel water depth, channel flow velocity and nitrate concentration. Nitrate  
9 concentration affects in-stream denitrification by the way of uptake velocity, i.e., uptake  
10 velocity decreases with the increase of nitrate concentration (Mulholland *et al.*, 2008). In our  
11 model constant uptake velocity is assumed, so the effect of nitrate concentration is not  
12 incorporated explicitly. We thus focus on the impacts of channel discharge on in-stream  
13 denitrification of NO<sub>3</sub>-N, as shown in Figure 13. According to Eqns. (9) - (11), the rate of in-  
14 stream denitrification increases with the channel length and decreases with the channel water  
15 depth and flow velocity. Figure 13 shows a significant seasonality of in-stream denitrification  
16 efficiency. The denitrification efficiency is defined here as the percentage of in-stream flux  
17 removed by in-stream denitrification per unit channel area (channel area = local channel  
18 length×channel width). It is highest in August when the channel water depth and flow  
19 velocity are smallest, and lowest in May when the channel water depth and flow velocity are  
20 largest. As for the spatial variability of in-stream denitrification, it is more significant in  
21 headwater channels than in downstream channels. Besides Big Ditch and Monticello stations,  
22 we add another location, Shively, located between Big Ditch and Monticello, in order to  
23 better present spatial variability of in-stream denitrification. Model results suggest that the  
24 most dominant factor for the predicted spatial variability of denitrification appears to be the  
25 local channel water depth. The water depth in headwater channels, which have small drainage

1 area contributing runoff, is much lower than that in downstream channels, which have large  
2 drainage areas contributing runoff into them. Channel water depth is also tightly related to  
3 flow velocity, i.e., usually the latter increases with the former giving fixed channel geometry.  
4 Therefore the in-stream denitrification efficiency is significantly higher in the channel near  
5 Big Ditch than those near Shively and Monticello. Channel length is another factor affecting  
6 in-stream denitrification efficiency. The local channel length corresponding to Big Ditch is  
7 18.3km, to Shively is 38.4km and to Monticello is 11.4km (estimated from DEM). In general,  
8 the longer the channel length, the longer the residence time of nitrate within the channel and  
9 therefore the higher the in-stream denitrification efficiency. In this case, however, the impact  
10 of channel length is apparently smaller than that of channel water depth in controlling the  
11 spatial variability of in-stream denitrification efficiency.

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## 12 **5 Summary and conclusions**

13 In this paper we have explored the coupled water and nutrient balances in a large tile-drained  
14 agricultural watershed in central Illinois, with the use of a distributed model based on the  
15 representative elementary watershed (REW) approach. The model was calibrated through the  
16 use of available time series data on streamflow at different gauging stations within the  
17 watershed and intermittent measurements of nutrient concentrations also at the same three  
18 stations. In addition, we compared average annual estimates of the various components of the  
19 runoff generation against two previous experimental studies, confirming that about 80% of  
20 the streamflow in the basin is carried by tile drain flows. Likewise, average annual estimates  
21 of the various components of the nutrient (N and P) balances were compared against estimates  
22 obtained from several previous experimental studies in the literature, and found good  
23 agreement. Once again, tile drains are found to be the carrier of over 90% of the riverine  
24 export of dissolved nutrients, especially nitrate. In the case of P, over 98% of the fertilizer

1 application is removed through grain harvest, and only a small fraction (less than 2%) is  
2 exported with runoff either in dissolved or particulate form. In the case of N, however,  
3 nitrogen fixation by plants represents 40% of the total annual inputs to the catchment (fixation  
4 + fertilization), of which slightly over 20% is exported with runoff mostly in dissolved form,  
5 predominantly by tile drain flow. The remainder is removed through grain harvest.

6 The coupled model was also used to gain insights into the interactions between hydrological  
7 and biogeochemical processes, and the role of climate and consequent hydrologic variability  
8 on nutrient export processes. The results showed that there is a very dependence on the  
9 strength of annual runoff and the annual export of nutrients, especially dissolved nitrate  
10 component. Assuming that nutrients inputs through fertilizer application is constant between  
11 years, and the observation that removal by grain harvest decreases only slightly with increase  
12 annual runoff, it is found that relatively dry years are characterized by nutrient accumulation  
13 in soil and relatively wet years are characterized by nutrient removal from soil storage. The  
14 net result of higher runoff and higher nutrient runoff in wet years and vice versa means that  
15 annual average nutrient concentration can be expected to stay relatively constant in such  
16 human-impacted agricultural regions. This phenomenon may be one of the causes of  
17 chemostatic behavior that has been reported in some agricultural regions of the world. This is  
18 not the case for phosphorus removal, however, since in this case the removal of phosphorus  
19 by runoff is minor comparing with the removal by harvesting.

20 This work has demonstrated that a parsimonious model of coupled water, sediment and  
21 nutrient balances can be developed that does justice to much of the multi-scale variability of  
22 hydrological and biogeochemical processes and their interactions, which are essential for the  
23 simulation and prediction of sediments and nutrients in large agricultural catchments. The  
24 model presented here can serve as a numerical framework, not only for making predictions of

1 the effects of climate and land use changes, but also to provide guidelines for undertaking  
2 new observations and new process studies that are critical for improving the predictive  
3 capability of such models in the future. Still, improvements are needed in several areas,  
4 including the transportation of phosphorous by tile drainage, an explicit treatment of nutrient  
5 uptake by vegetation (including varieties of food and biofuel crops and natural vegetation),  
6 and denitrification processes within the river network, including a more accurate  
7 representation of channel hydraulic geometry. Continuous measurements of nutrient  
8 concentrations in tile drains, river reaches at a range of scales and in the hillslopes are needed  
9 to improve process descriptions in the model and to validate the model predictions. This is left  
10 for future research.

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1 | Table 1 Nitrogen annual balance [Kg N /ha]

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	Expected	Simulated	Source / reference
NH4-N Fertilizer	95.0* <sup>1</sup>	-	McIsaac & Hu, 2004
NH4-N Deposition	5.0*	-	NADP/NTA Bondville Station (IL11)
NO3-N Deposition	4.8*	-	NADP/NTA Bondville Station (IL11)
NH4-N Fixation	51~62 <sup>1</sup>	65.3	McIsaac & Hu, 2004; Hu <i>et al.</i> , 2007
NO3-N Field Denitrification	10~23	10.9	David & Gentry, 2000; Howarth <i>et al.</i> , 1996; Hu <i>et al.</i> , 2007
NH4-N Volatilization	5.0	4.9	McIsaac & Hu, 2004
NO3-N Riverine Denitrification	5.2 <sup>2</sup>	5.8	David & Gentry, 2000; Howarth <i>et al.</i> , 1996
NO3-N Riverine Export	25.8	29.1	McIsaac & Hu, 2004
TKN	3.5	3.2	McIsaac & Hu, 2004
Grain Export	116.0	115.8	McIsaac & Hu, 2004

2 \* Model inputs

3 <sup>1</sup> It is assumed that 50% of the study area is planted corn, and another 50% is soybean. NH4-N  
4 fertilizer is only applied to the corn field. So this value is in fact half of what will be applied to a corn  
5 field.

6 <sup>2</sup> Estimated as 20% of riverine flux.

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1 Table 2 Phosphorous annual balance [Kg P /ha]

	Expected	Simulated	Source / reference
P2O5-P Fertilizer	30*	-	Greg McIsaac (personal communication)
PO4-P Deposition	0.04*	-	NADP/NTA Bondville Station observation (IL11)
DP Riverine Export	0.3~0.55	0.30	Gentry et al., 2007; David & Gentry, 2000
PP Riverine Export	0.3~0.55	0.31	Gentry et al., 2007 ; David & Gentry, 2000
Grain Export	28.9~29.4 <sup>1</sup>	29.6	

2 \* Model inputs

3 <sup>1</sup> Estimated according to mass balance

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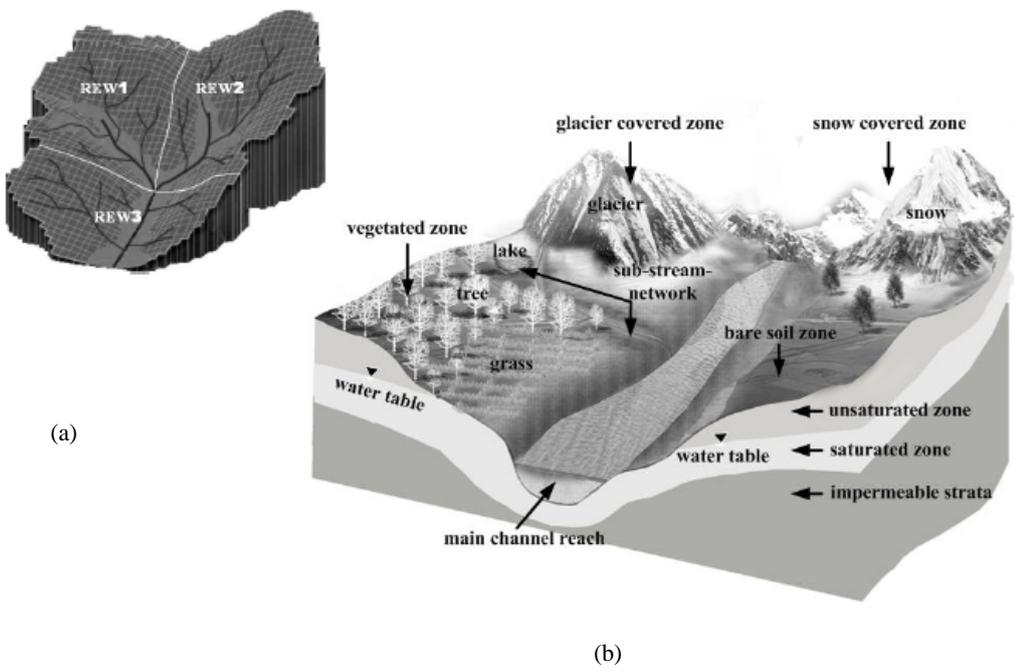


Figure 1. Spatial delineation in THREW model. (a) A basin is divided into a number of representative elementary watersheds (REW). (b) Each REW is further divided into several sub-zones.

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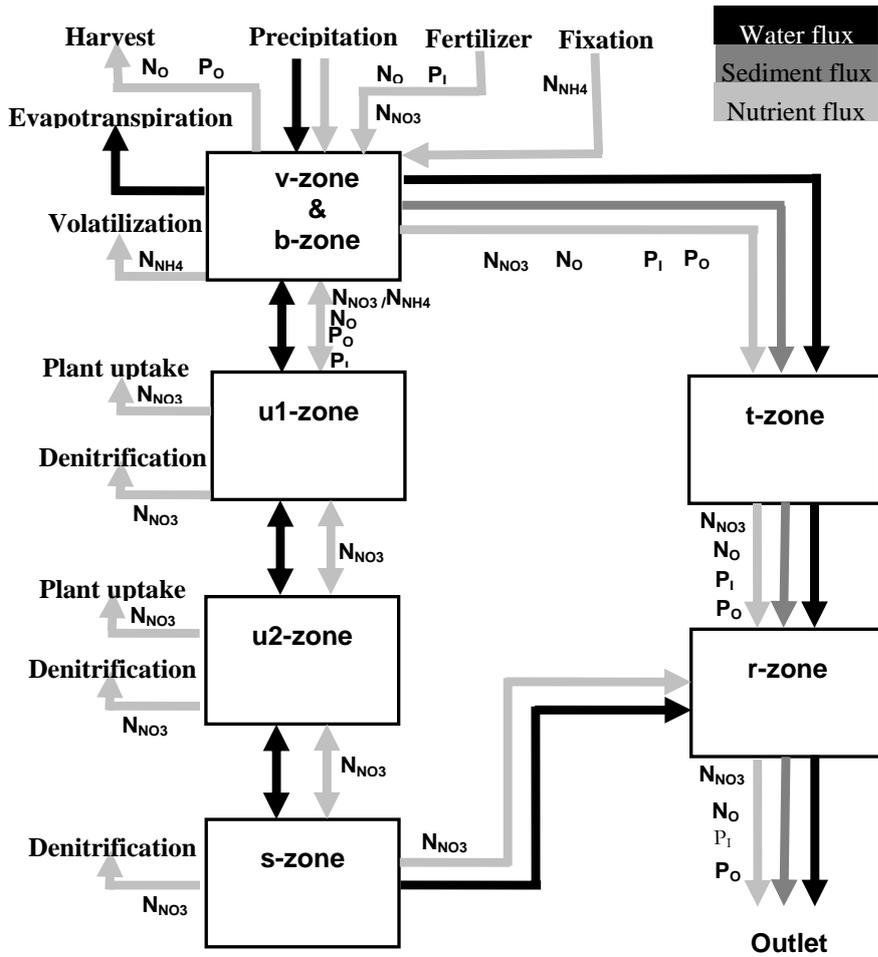


Figure 2. Conceptual illustration of coupled water, sediment and nutrient modeling in THREW.  $P_I$  represents inorganic dissolvable phosphorous.  $P_O$  represents organic phosphorous and soil-absorbed inorganic phosphorous.  $N_O$  is organic nitrogen.  $N_{NO_3}$  is nitrate.  $N_{NH_4}$  is ammonium.

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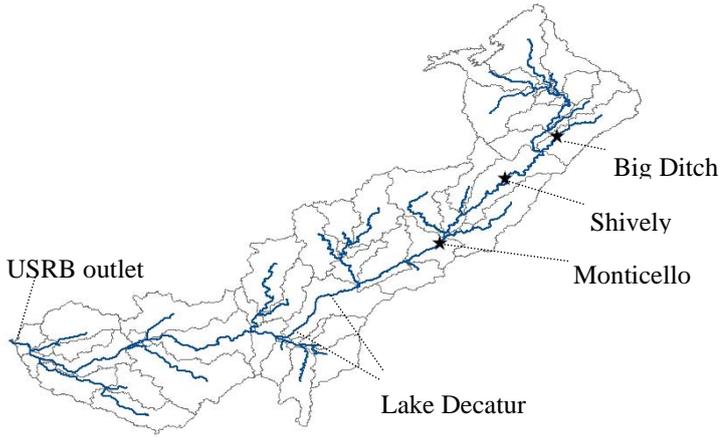
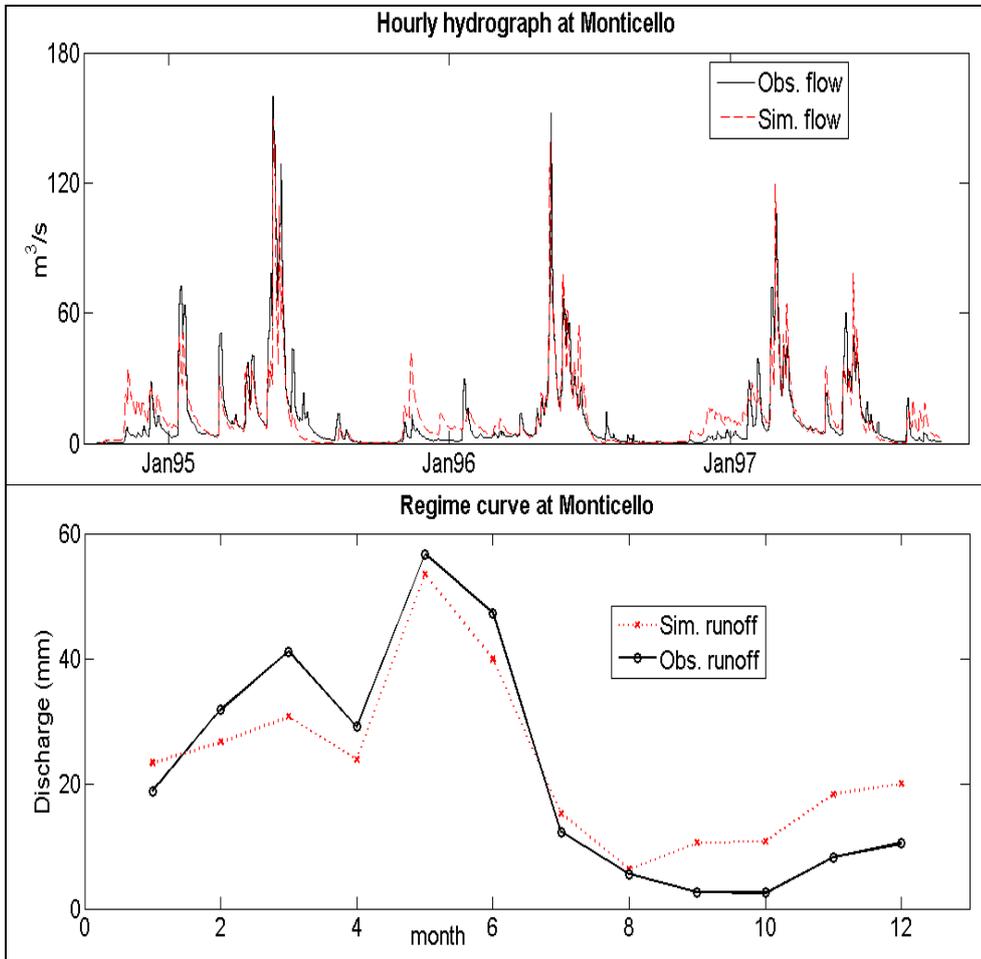
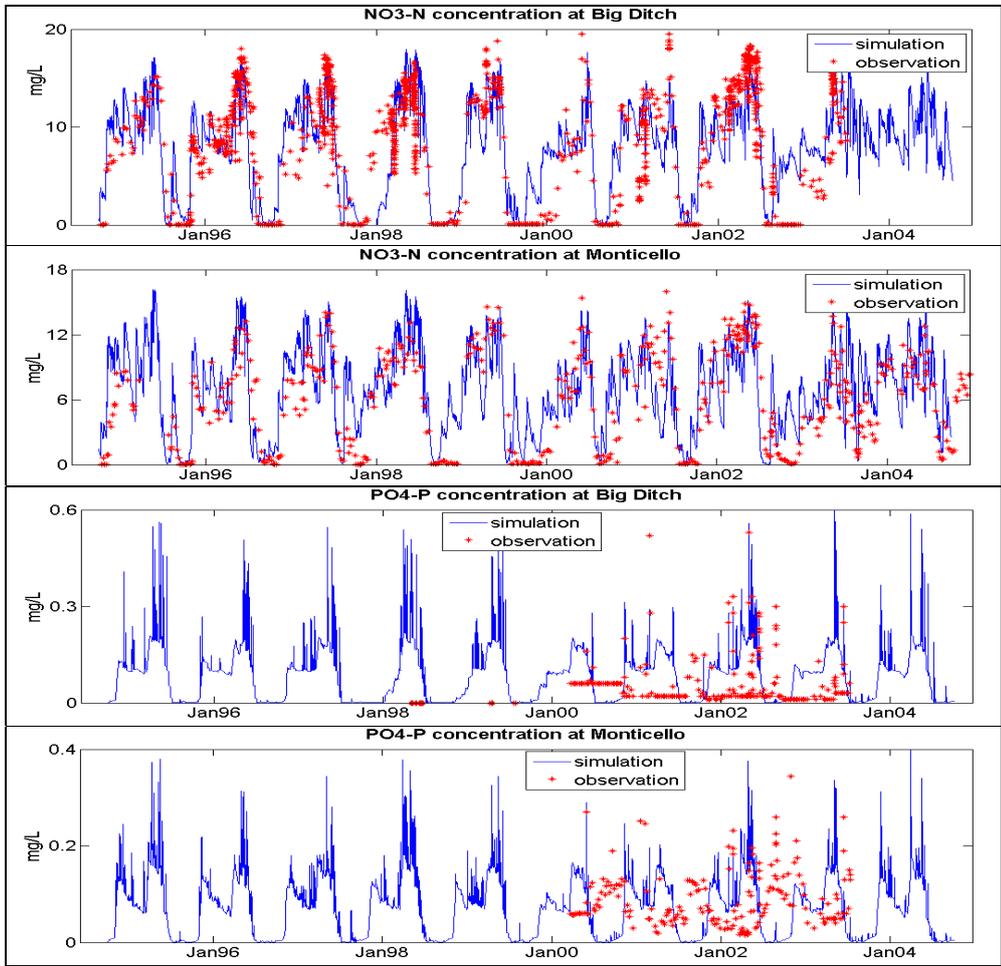


Figure 3. Upper Sangamon River Basin (USRB) and the delineation of REWs



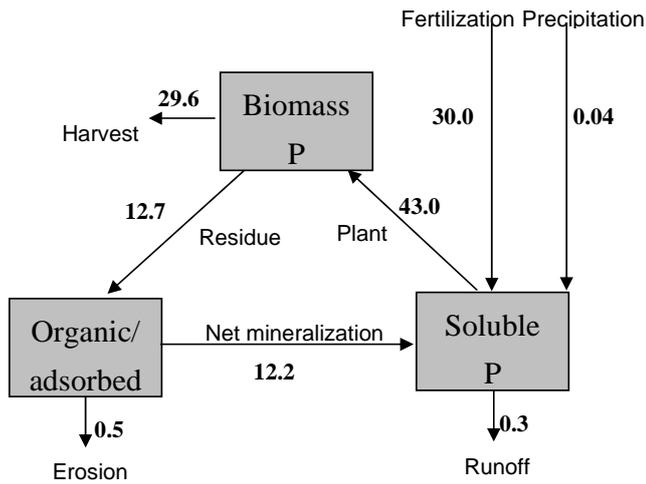
1 Figure 4. Comparison of the model predicted and observed runoff response at Monticello. The  
 2 regime curves are normalized by the total upstream drainage area of Monticello.  
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1 Figure 5. Comparison between the predicted and observed nitrate and phosphate  
 2 concentration series. The simulated NO<sub>3</sub>-N and DP concentration series are at hourly scale;  
 3 while the observed series are at irregular intervals, most biweekly. There is no observation  
 4 some time.

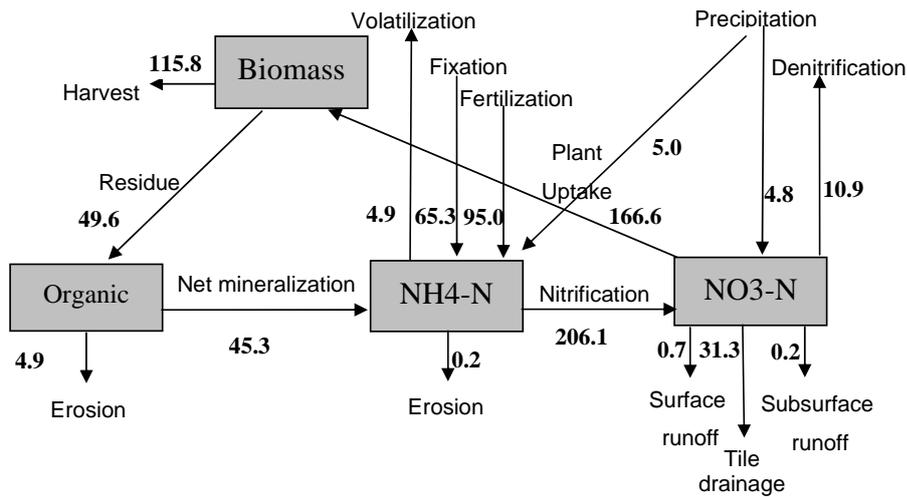
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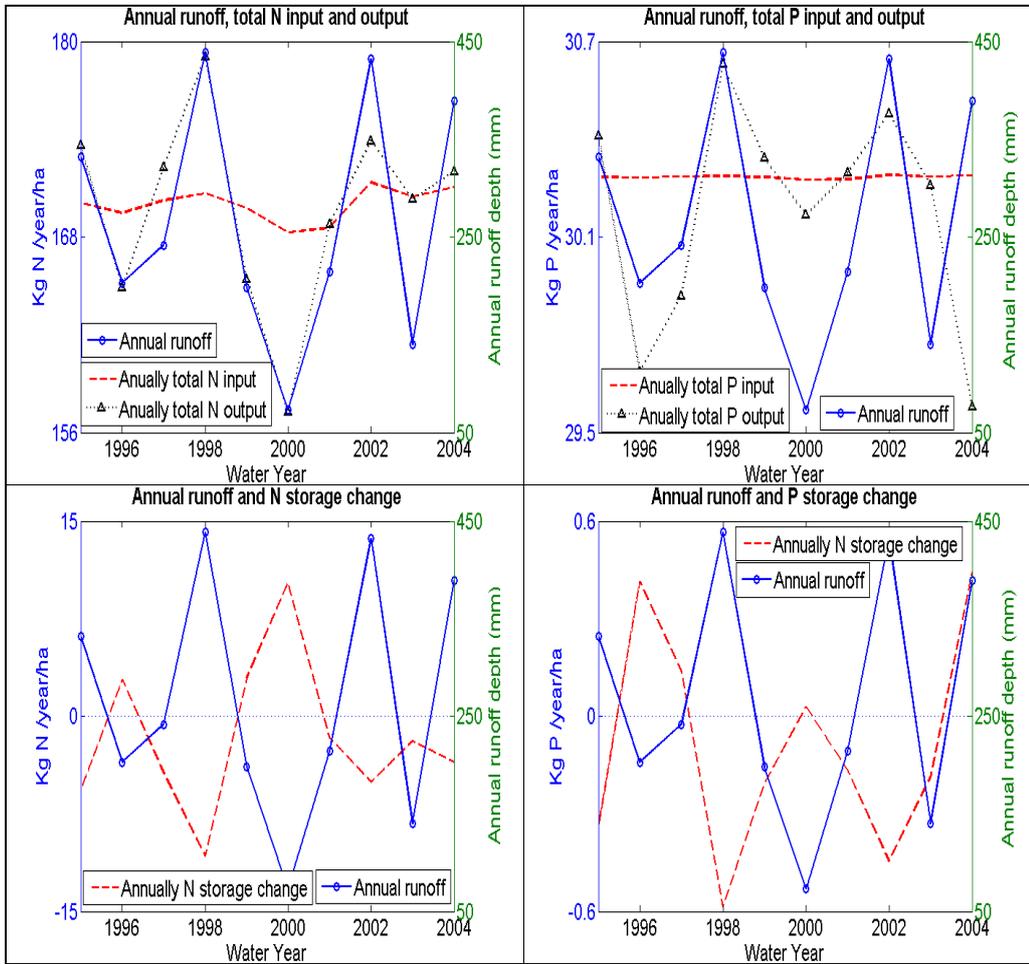


9 Figure 6. Simulated phosphorous cycling (all values are in Kg. P/ha/yr, averaged through the  
10 drainage area of Monticello station)

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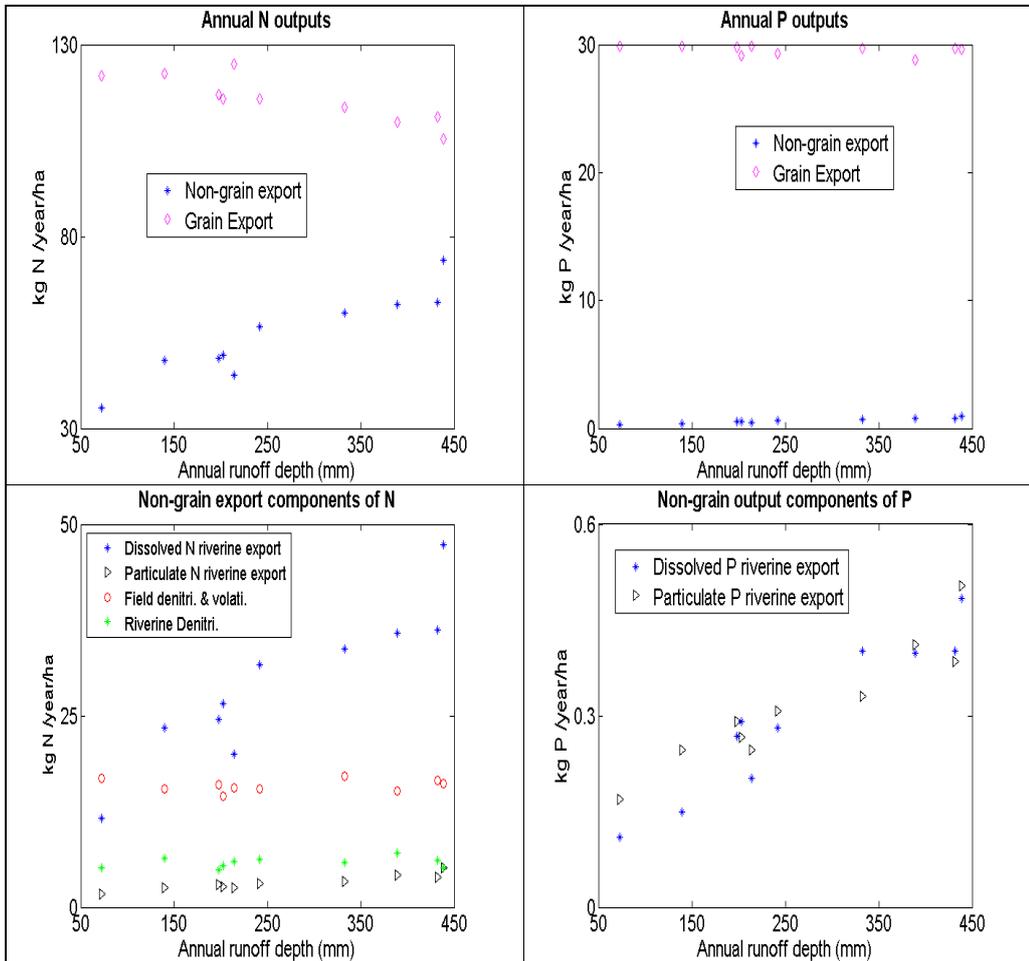


22 Figure 7. Simulated nitrogen cycling (all values are in Kg. N/ha/yr, averaged through the  
23 drainage area of Monticello station)

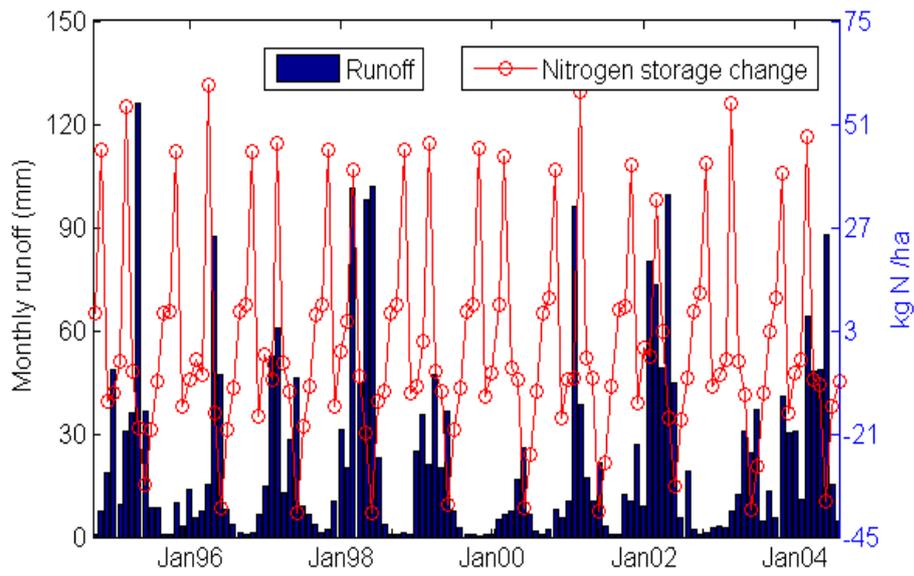


1 Figure 8. Annual runoff, annual input, output and storage change of nitrogen and phosphorous.

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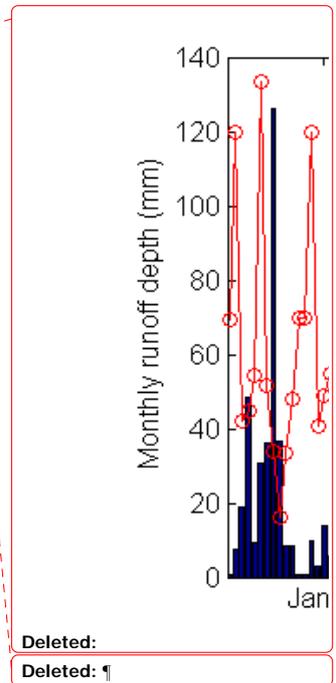


1 Figure 9. Interactions between hydrological and biochemical processes at the annual scale  
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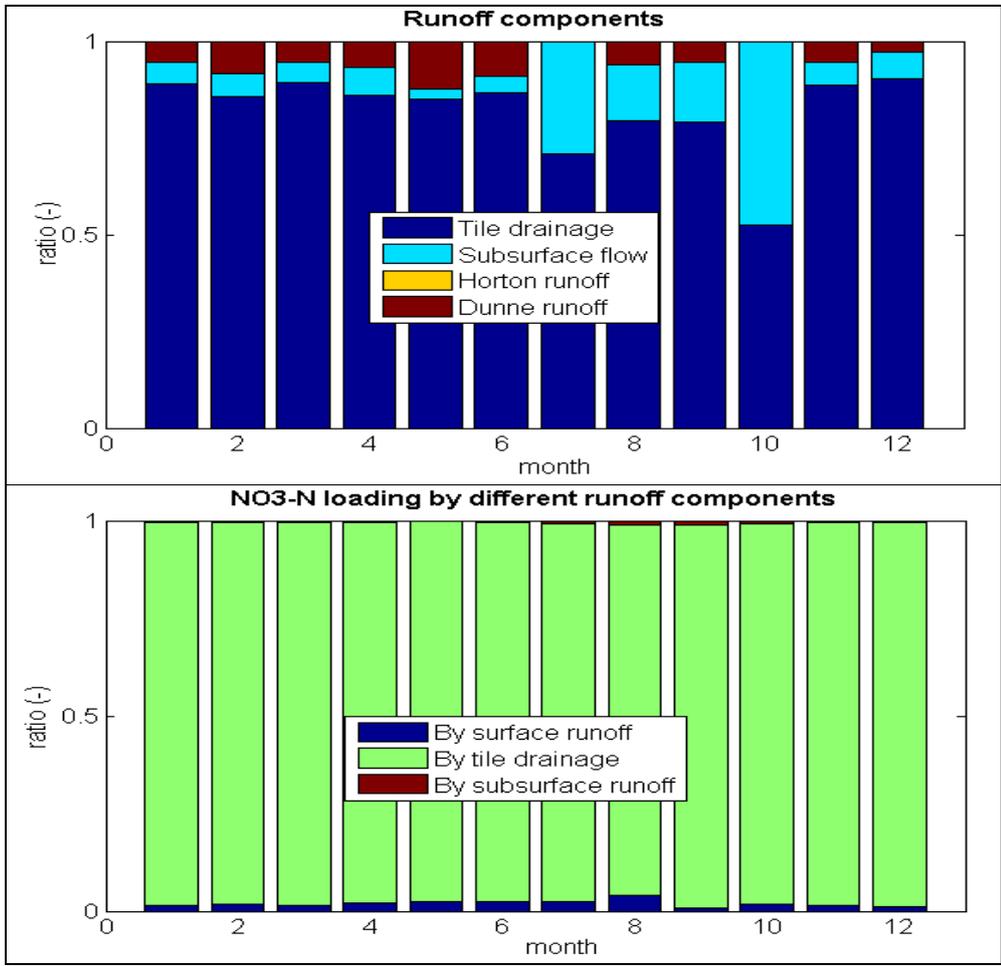


1 | Figure 10 Interactions between hydrological and biochemical processes at the monthly scale

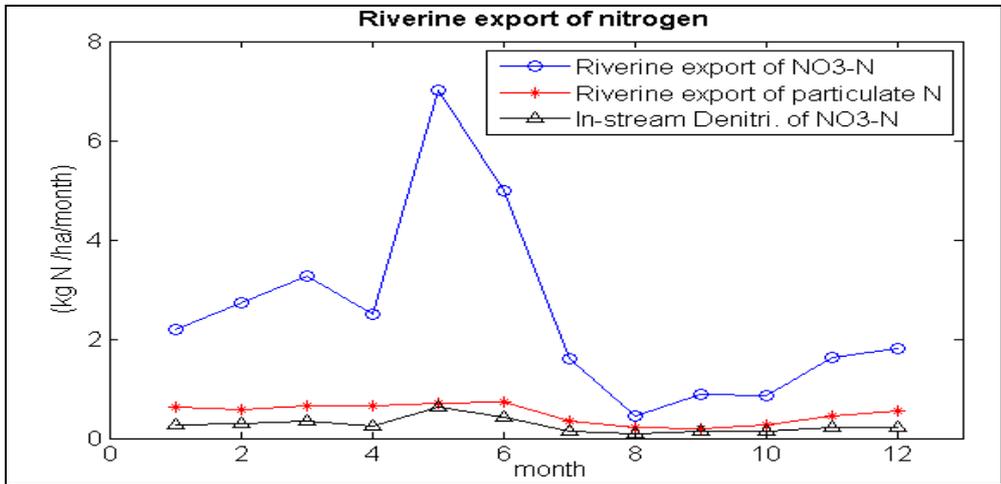
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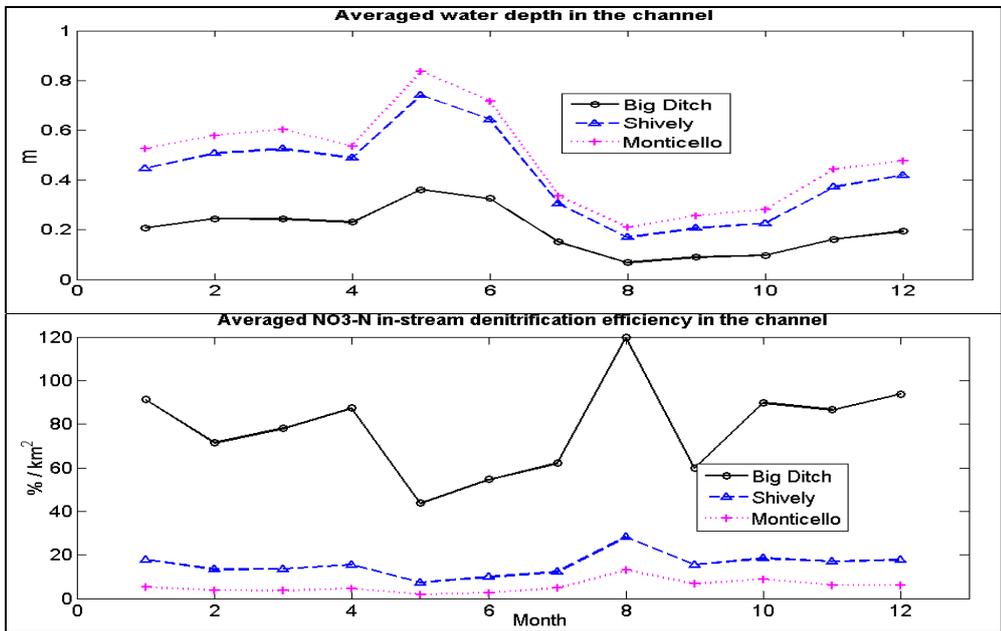


1 Figure 11. Seasonal variation of runoff components and the loading of NO3-N by different  
 2 runoff components. All values are averaged through the upstream area of Monticello.  
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1 Figure 12. Seasonal variation of riverine export of nitrogen.

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5 Figure 13. Seasonal variation of channel waterdepth and in-stream removal efficiency (for the  
6 local channel reach corresponding to each station). The in-stream removal efficiency is  
7 defined as the percentage of in-stream flux removed per unit area of channel by in-stream  
8 denitrification, estimated as  
9  $NO_3-N$  in-stream removal / (upstream inflow + lateral hillslope inflow) / channel area

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