An integrated framework to model nitrate contaminants with interactions of agriculture, groundwater, and surface water at regional scales: The STICS–EauDyssée coupled models applied over the Seine River Basin

Ahmad Tavakoly, Florence Habets, Firas Saleh, Zong-Liang Yang, Cyril Bourgeois, David R. Maidment

*Title Page

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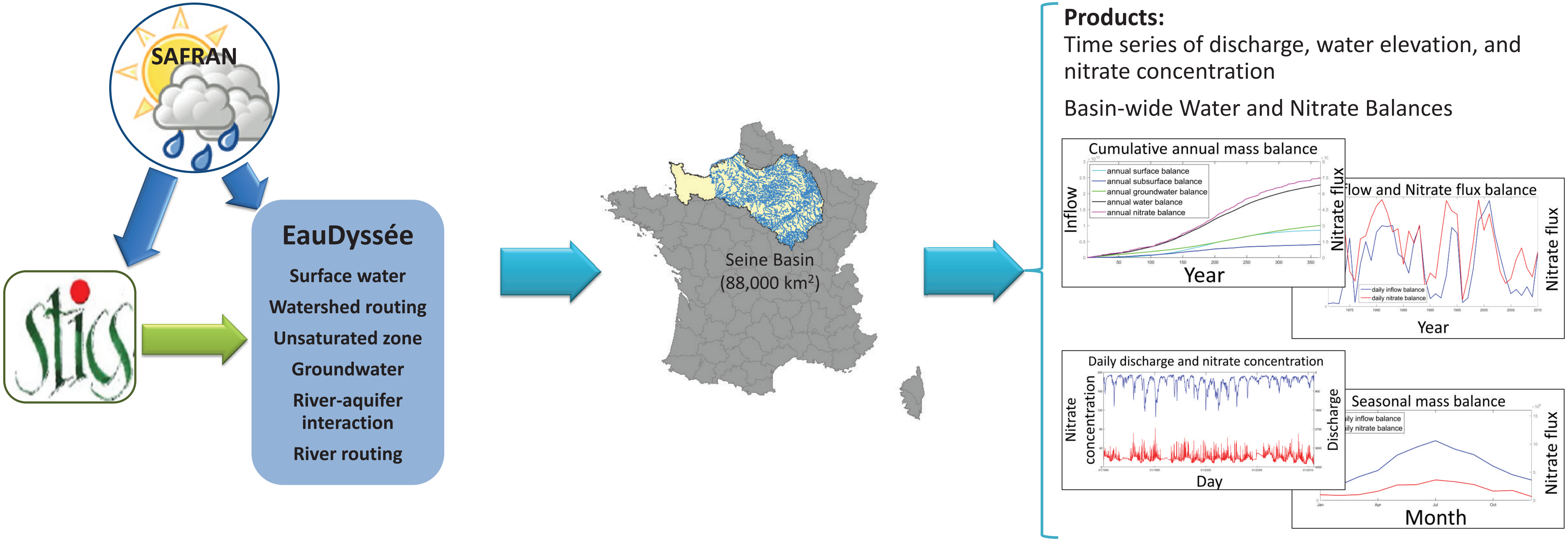
*Graphical Abstract



*Highlights (for review : 3 to 5 bullet points (maximum 85 characters including spaces per bullet point)

Highlights

- Agronomic and distributed hydrologic models were coupled considering aquifer and river interaction
- Daily nitrate flux and riverine concentration were simulated for 39 years
- Simulated nitrate flux depends on the inflow produced by surface and subsurface
- Regional hydrologic modeling improves estimation of nitrate concentration
- Nitrate load to rivers increased during wet season and decreased during dry season

An Integrated Framework to Model Nitrate Contaminants with Interactions of Agriculture, Groundwater, and Surface Water at Regional Scales: The STICS–EauDyssée Coupled Models Applied over the Seine River Basin

Ahmad A. Tavakoly*
Research Hydraulic Engineer, U.S. Army Engineer Research and Development Center, Coastal and Hydraulics Laboratory

Florence Habets
Sorbonne Universités, UPMC, Univ Paris 06, CNRS, EPHE, UMR 7619 METIS, Paris, France

Firas Saleh
Stevens Institute of Technology, Davidson Laboratory, Department of Civil, Environmental and Ocean Engineering, Hoboken, NJ 07030, USA

Zong-Liang Yang
Department of Geological Sciences, Jackson School of Geosciences, The University of Texas at Austin

Cyril Bourgeois
Centre International de Recherche sur l'Environnement et le Développement, Nogent-sur-Marne, France

David R. Maidment
Department of Civil, Architectural, and Environmental Engineering, The University of Texas at Austin

***Corresponding author**

Ahmad A. Tavakoly, Ph.D.

5825 University Research Court, Colege Park, MD 20740

Ahmad.A.Tavakoly@erdc.dren.mil

Abstract

Nutrient enrichment from natural and anthropogenic activities is one of the major environmental pollution stressors. Nitrogen is one of the main reasons for failure to achieve a good quality for the groundwater bodies in river basins. This study presents an integrated framework that couples an agronomic model (STICS) and a distributed hydro(geo)logic model (EauDyssée) to estimate nitrogen fluxes in the hydrosystem at the regional scale. The EauDyssée modeling framework was enhanced to include nitrate transport from soils to rivers via surface runoff and the onwards transport from aquifers to rivers. Furthermore, an in-stream nitrate model to simulate nitrate concentration in the river network was implemented in the framework. The utility of the integrated framework was demonstrated on the Seine River Basin with an area of 88,000 km^2, a complex hydrosystem with multiple aquifers, and one of the most productive agricultural areas in France that encompasses the megalopolis of Paris. The STICS-EauDyssée framework was implemented for a long-term simulation covering 39 years (1971-2010). Comparison of groundwater nitrate concentrations with observations showed an overall absolute bias of less than 10 mg/l. Model results showed that simulated nitrate fluxes to rivers highly depend on the inflow produced by surface and subsurface waters. Simulated in-stream nitrate concentration also compared well with observations, particularly in the eastern region of the Seine River Basin. In general, results showed that a long-term simulation of nitrate contaminant with the combined STICS-EauDyssée system was satisfactory at the regional scale. This work can benefit decision makers to formulate management strategies and Agri-environmental measures to mitigate pollution from agricultural activities to the river system.

Keywords: Nitrate flux; Surface-aquifer interactions; Regional scale modeling; Seine River Basin; Distributed hydrologic modeling; STICS

1-Introduction

Increasing nitrate concentration in surface water and groundwater is a major concern of water quality protection and consequently water resources management (Hooda et al., 1997; Kampas and White, 2003; Vitousek et al., 1997). Anthropogenic activities including food and energy productions have greatly increased nitrogen creation by over a factor of 10 compared to the late-19th century (Galloway et al. 2004). The excess nitrate causes eutrophication and adverse environmental effects such as harmful algal blooms (growth of phytoplankton in a water body), hypoxia (oxygen depletion), and reduction of fish and shellfish production (Oehler et al., 2009; Sebilo et al., 2003; Spalding and Exner, 1993; Wade et al., 2005; Zhang and Schilling, 2005). Climate change also has impacts on water quality. Changes in water discharge, velocity which controls the residence time, water temperature, and precipitation are climate change factors which can enhance nutrients (Ducharne et al., 2007; Sinha et al., 2017). Increasing of water temperature can intensify biological activity and consequently nutrients (Ducharne 2008). Using 21 different CMIP5 (Coupled Model Intercomparison Project Phase 5, Taylor et al., 2012) models, Sinha et al., (2017) showed that the amount of riverine total nitrogen load will be increased by $19 \pm 14\%$ in the United States based on the precipitation changes. Therefore, developing a predictive capability of modeling nutrients transport is imperative to understand the effect of climate change, and human activities on nitrogen changes at regional and global scales.

Before releasing nitrogen to the surface water, soil and groundwater have capacity of nitrogen retention (nitrogen removal, Grizzetti et al., 2015). Nitrogen retention can occur in the soil through denitrification process at the water saturated condition. Nitrogen denitrification and accumulation can also take place in aquifers at the anoxic condition (dissolved oxygen is depleted in groundwater). Aquifer permeability may also affect residence time of nitrogen and attenuation in groundwater. Accordingly, sustainable development and comprehensive water management require the need for the full representation of nitrate contamination from the soil surface to the unsaturated zone, groundwater, and rivers for the entire basin. In terms of nutrient modeling at the reginal scales, a few models are introduced. Soil and Water Assessment Tool (SWAT) is a commonly-used semi-distributed, continuous-time watershed model that predicts the impact of land management on water, sediment, and chemical yields in ungagged watersheds (Arnold et al. 1999). The model has a limitation to account for all sources of nitrogen such as atmosphere (Alexander et al. 2002) and to determine point sources of N-inputs (Kunkel et al., 2017). STONE uses one-dimensional physicaly based model to simulate N and P fluxes in surufuce and groundwater and vertical trasnport of N between saturated and unsaturated top-soil layers (Wolf et al., 2005). This model was used to analyze the impcat of farming practices and to evaluate environmental policies on nutrient emission over the Netherlands. MIKE SHE is a fully distributed model and uses numerical solutions while solving the flow equations. As a consequence, the model is computationally expensive and hence not adequate for large watersheds (Borah and Bera 2003; Daniel et al. 2011). Other models such as the GROWA-DENUZ-WEKU model system uses six diffuse input pathways (erosion, drainage system, interflow, groundwater, wash-off, and atmospheric deposition) to determine the N input into groundwater and surface water (Kunkel et al., 2004). This model is the most common model system used in Germany at the level of river basins and Federal States (Kunkel et al. 2017; Kunkel and Wendland 1997, 2002). The GROWA component of this model system uses empirical approach to calculate long-term availability of water resources. To reduce the computational cost, the GROWA model uses coarse temporal resolution (≥ 1 year) for climatic input data (Kunkel and Wendland 2002).

Considering the interactions of surface water and groundwater is vital to understand nitrate changes in the hydrosystem (Baratelli et al., 2016). Flipo et al., 2014 conducted an extensive literature review of distributed physically based models. According to their study, only 19 of 183 publications were at the regional scale (> 10,000 km^2) where two of them considered stream-aquifer exchanges (Monteli, 2011 and Pryet etal., 2015). Moreover, Baratelli et al., (2016) showed that considering the river stage fluctuations improve the accuracy of the discharge modeling and the assumption of constant river stage can result to a significant underestimation of total infiltration and exfiltration at the regional scale. The sensitivity study was conducted using the EauDyssée platform (Pryet et al., 2015; Saleh et al., 2011) in their study. This platform includes in-stream water level fluctuations and an explicit quantification of the stream-aquifer exchanges.

The research proposed herein incorporates hydrological modeling system and agronomic model to improve understating of the nutrient dynamics in surface water and groundwater interaction and in streams over large scale river networks and long-term time periods. For this purpose, the EauDyssée platform with its unique aforementioned capabilities was applied and developed to simulate nitrate contaminants. Coupling of the EauDyssée model and the agronomic model STICS (Simulateur mulTIdisciplinaire pour les Cultures Standard, Beaudoin et al., 2016; Brisson et al., 1998, 2002), to obtain the infiltrating nitrate flux leaving the root zones is presented. Furthermore, this study shows the application of streamflow results from a large scale river routing model to simulation nitrate at the reginal scale. The modeling system was implemented over the Seine River Basin in France. Due to increasing nitrate concentrations over time, the Seine River Basin represents an ideal test bed of river nutrient chemistry in a regional ecosystem. In 2013, most of the surface and groundwater bodies of the Seine River Basin did not have such a desirable status, mostly due to nutrients in the groundwater bodies (AESN, 2013). Nutrient enrichment and eutrophication are major environmental phenomena in the French coastal zone. Many studies have investigated the nitrogen cycle of the Seine River Basin with different purposes. Some studies focused on the nutrient transfers for a portion of or the entire Seine River Basin, but did not explicitly include stream-aquifer interaction (Billen et al., 2007; Cugier et al., 2005; Even et al., 2007; Garnier et al., 2005; Passy et al., 2012; Sebilo et al., 2003; Sferratore et al., 2005; Thieu et al., 2009, 2010). Other studies only considered the aquifers (Bourgois et al., 2016; Ledoux et al., 2007; Philippe et al., 2011; Viennot, 2009), and some complete studies only encompassed smaller parts of the Seine River Basin (Flipo et al., 2007a; 2007b), which can support the understanding of nutrient transformations.

This study describes simulation of nitrate flux leaching into the river network and consequently to compute in-stream nitrate concentration for the entire Seine River Basin, including several layers of aquifers over 39 years (1971-2010). Transport of nitrate from land to rivers and from aquifers to surface water and rivers were added to the EauDyssée platform. Taking the leaching nitrate from EauDyssée and streamflow simulations, first order solute transport model was also developed to simulate in-stream nitrate concentration at the regional scale. The new enhancements allow the EauDyssée platform to simulate regional watershed flow and solute modeling with stream and aquifer interactions.

2- Materials and Methods

2-1-Study Area

The Seine River Basin covers an area of approximately 88,000 km^2 in northern France (Figure 1). The Seine River is 776 km long and has 25,000 km of tributaries (Table 1). It begins at an elevation of 446 m at Source-Seine in the department of Côte-d'Or in Burgundy and discharges into the English Channel near the city of Le Havre. Table 1 shows that the stream gradients are not extremely varied; although elevation ranges from 0 to 856 m above sea level, with 90% of the basin is below 300 m. The hydrological regime of the Seine River Basin is considered to be pluvial oceanic, with varied seasonal flows (high flows in winter and low flows in summer) that reflect rainfall distribution throughout the year. The Seine River Basin also has several aquifers that play an important role in sustaining base flow (Rousset et al., 2004). Interactions of three major aquifers with the river network were considered in this study. These aquifers are from top to bottom: 1) Oligocene; 2) Middle and lower Eocene; and 3) Upper-Cretaceous chalk (Gomez et al., 2003b). The aquifers are relatively permeable (from medium to high), and are relatively vulnerable (from medium to high). The middle and lower Eocene is composed of coarse limestones of Lutetian and sands. The total transmissivity varies from 5 to 10^{-4} m^2/s. The Upper-Cretaceous chalk aquifer has a porosity between 37 and 45% and a transmissivity less than 10^{-2} m^2/s. A full description of the Seine aquifers is available at http://sigessn.brgm.fr/spip.php?rubrique5.

Table 1: Mean and total morphological characteristics of the Seine River Basin from the river network Carthage.

Stream Order	Number	Mean		Total	
		Width (m)	Slope (m/m)	Length (km)	Catchment area (km^2)
1	2,887	2.5	0.0151	11,714	42,234
2	1,440	5.9	0.0062	5,591	17,190
3	848	12.6	0.0034	3,801	12,493
4	354	23.0	0.0022	1,932	6,982
5	186	50.2	0.0014	1,102	4,497
6	115	88.9	0.0013	601	2,416
7	36	200.9	0.0011	383	2,113
Entire Seine River Network	5,866	10.5	0.0097	25,124	87,926

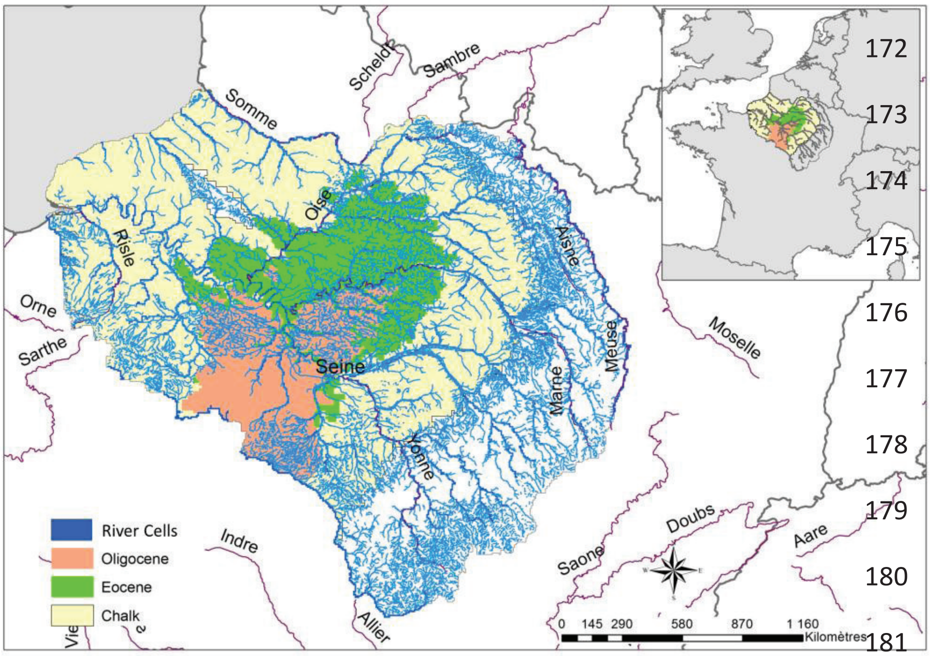


Figure 1: The Seine River Basin including the river network and its main aquifers.

The Seine River Basin is predominantly covered by an intensive agricultural industry with up to 57% of the land surface allocated to agriculture (Mignolet et al., 2007), which is the main source of nutrients entering rivers in Europe (De Wit et al., 2002). The rest of the basin is covered by forest (25%), grassland (13%), and urban (5%). The center of the basin dominantly covered by cereal, oilseed, and sugar beet croplands. The outer limit of the basin is mostly covered by forest and grassland (Garnier et al., 2009; Sferratore et al., 2005). The Seine River Basin is home to approximately 20 million inhabitants, including 10 million people in the region of Paris. Agricultural activity, pollution sources, and population density lead to water quality degradation and nutrient enrichment of the Seine River Basin. Furthermore, this basin includes a major aquifer system made by a series of connected aquifer layers that interact with surface water resources and are key components of the hydrological and biogeochemical processes of the area (Contoux et al., 2013; Gomez et al., 2003b).

2-2-Descriptions of Models

This research is based on the coupling of an agronomic model, STICS, and a regional hydrological model, EauDyssée over the entire Seine River Basin. The meteorological forcing data for EauDyssée includes precipitation and potential evapotranspiration which are produced by a mesoscale atmospheric analysis system, Météo-France SAFRAN (Durand et al., 1993; Quintana-Seguí et al., 2008), at a daily time step over a regular 8-km grid.

2-2-1-The STICS Crop Model

STICS (Brisson et al., 2003) is a process-based daily time step crop model that simulates (a) crop yields in terms of quantity and quality and (b) the environment in terms of drainage and nitrate leaching. STICS is able to: adapt to various crops using the same set of equations and specific parameters, simulate various climate and soil conditions, add new modules, and communicate externally with other models and developers. The input variables are related to climate, soil, and the crop system (Schnebelen et al., 2004). The upper boundary corresponds to climatic variables including solar radiation, daily minimum and maximum temperatures, precipitation, and reference evapotranspiration. The lower boundary corresponds to the soil/sub-soil interface. The core of the STICS model includes four primary sets of modules. The first set of modules includes phenology, shoot growth, and yield formation. This set considers the ecophysiology of aerial plant parts. The second set contains four modules (root growth, water balance, nitrogen balance, and soil transfer) that simulate the interaction between underground plant parts and soil functions. The third module is crop management, which accounts for water transfer through the canopy, the status of water and heat balances in the soil-crop system, and fertilizers. The fourth module is the microclimate, which calculates temperature and air humidity through the canopy.

Three principal databases are used in the STICS model to characterize the pedology, meteorology, and agriculture of the Seine River Basin. The three databases are: soil, agriculture, and meteorological; each has a different spatial resolution (Beaudoin et al., 2016; Ledoux et al., 2007). The intersection of these databases generates spatial units called General Simulation Units (GSU) that share the same spatial, pedological, agricultural, and meteorological characteristics. STICS was made up of 9596 units with an average unit area of 12 km^2 over the Seine River Basin. The dominate nitrogen process in the Seine Basin is nitrate due to the majority covering of the landscape with clear-cut forest and agricultural system (Billen et al., 2007). Consequently. The STICS model has been extensively used as an agronomical model in this basin. The nitrogen flux estimated by STICS on the Seine River Basin was recently assessed by Beaudoin et al., 2016.

2-2-2-The EauDyssée Platform

The EauDyssée modeling platform is a hydrometeorological and biogeochemical model based on the existing models and databases of the PIREN-Seine program. The hydrogeological component of the model uses the same principles as the MODCOU model (Habets et al., 2008; Ledoux et al., 1989). EauDyssée couples existing specialized modules to simulate water resources (quantity and quality) at regional scales (Figure 2): the surface component, the river routing component, the unsaturated component, and the groundwater dynamic or saturated component (Philippe et al., 2011; Pryet et al., 2015; Saleh et al, 2011).

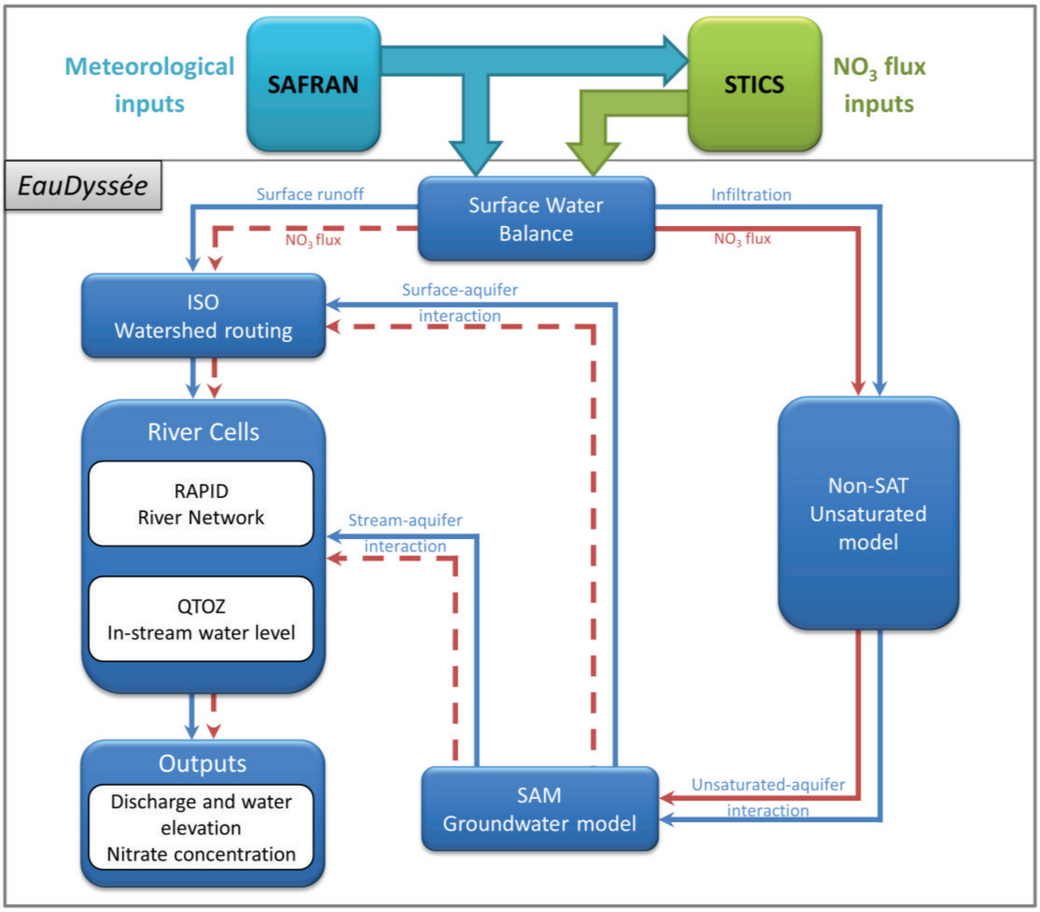


Figure 2: Schematic representation of coupling among SAFRAN, STICS, and EauDyssée. The solid blue line represents an existing coupling system between modules for flow simulations in the EauDyssée platform. The solid red line shows an existing NO_3 flux simulation from surface to Non-SAT and from Non-SAT to the SAM groundwater model prior to this study. The dashed red line represents NO_3 flux simulation added in this study.

The surface component of EauDyssée uses a seven-parameter conceptual model to compute water mass balance at a daily time step for each cell of the surface mesh (Deschesnes et al., 1985). In this module, the domain is divided into units called production functions that are generated based on the interaction of land-use and geological units (Golaz-Cavazzi et al., 2001; Gomez et al., 2003a). Inputs to the surface component are precipitation and potential evapotranspiration with a daily time step provided by SAFRAN. The outputs are actual evapotranspiration (AET), surface runoff, infiltration, and soil storage. The total number of surface cells covering the Seine River Basin is 35,698 with an average resolution of one square kilometer. The ISO module is used to route surface runoff to the river network. A number of isochronal zones, representative of the number of travel time steps, are defined in the ISO module to determine the delay between runoff generation and the time that runoff reaches the nearest river cell.

EauDyssée incorporates a river network model called Routing Application for Parallel ComputatIon of Discharge (RAPID) in the river network component (David et al., 2011b) and a module to estimate river water level fluctuation called QtoZ (Saleh et al., 2011). Inclusion of RAPID allows a direct computation of flow for each river cell of the quad tree river network and flexibility in the number and location of river gages. The QtoZ module improves river-aquifer interaction by taking into account river water level fluctuations. Application of the RAPID model in the SIM-France model was discussed by David et al. (2011a). The RAPID model has been extensively applied in the United States (e.g. David et al., 2013; Follum et al., 2016; Tavakoly et al., 2012, 2016a, 2016b). Inputs to RAPID are surface and subsurface runoff generated by the ISO module, and outputs are streamflow in each cell of the grid river network. Discharge computed by RAPID is used by the QtoZ module to calculate water levels at a given river cell in the EauDyssée platform. At each time step QtoZ computes a water level that is sent to the groundwater model (SAM) to simulate stream-aquifer interactions. QtoZ has three options for calculating water levels: (a) fixed water level, (b) rating curve, and (c) the Manning equation. Taking streamflow simulated by the RAPID model, the Manning equation option was modified in this project to estimate flow velocity and cross-sectional area for each river cell at every time step.

Infiltration is vertically portioned by the production function transferred to groundwater within the unsaturated zone. The unsaturated zone component, NONSAT (Ledoux et al., 1989), consists of Nash reservoir cascade (Nash, 1960). The number of reservoirs depends on the distance between soil horizons and the saturated zone, which is initially calculated on the basis of hydraulic head distribution. Prior to this study, NONSAT was adapted to transfer solute components (Gomez et al., 2003a; Philippe et al., 2011).

The groundwater component SAM (Simulation of Multilayer Aquifers) is a regional spatially-distributed model that applies the diffusivity equation to compute both the temporal distribution of hydraulic heads and the flow in multilayer aquifer units (Ledoux et al., 1989; Marsily, 1986). SAM computes the water flux exchanged between aquifer and stream grid-cells using water levels calculated by the QtoZ module and river volumes calculated by RAPID. SAM also simulates the diffusive transfer of passive solute (Bourgeois et al., 2016; Ledoux et al., 2007; Philippe et al., 2011). The three aquifers version of the EauDyssée platform was first established by Gomez et al., (2003b). The model was previously used to study climate change impact on the rivers and groundwater (Habets et al., 2013). Assessment was based on over 130 wells, with a bias lower than 1m for fifty percent of them. In this study, the EauDyssée platform was enhanced so that contaminants such as nitrate can be routed to the river. Improvements are explained in the following section.

2-2-3-Developments in the EauDyssée Platform to Simulate Surface and Stream-Aquifer Nitrate Exchange

Developments of the nitrate simulation in this study are illustrated with dashed red in Figure 2. The solute transport was added to watershed routing within the surface component of the EauDyssée platform. The ISO module (Figure 2) routes runoff to the river network with the association of the isochronal zones. The ISO module is modified to accumulate the mass of solute constituents and define the total mass transferred to river cells. A new module called "ISO solute", was added to the EauDyssée platform to model watershed solute transport and to provide nitrate flux leaching to river cells. The ISO solute module has the advantage of including the solute flux received from the aquifer in addition to the solute transport from surface runoff. The solute transport with the stream-aquifer interaction was developed based on the approach used to simulate stream-aquifer exchange flow in the EauDyssée platform. The flow exchange between the stream and the aquifer is computed based on the difference of hydraulic heads for river cells and associated aquifer cells (Rushton, 2007):

$$Q_r = R_C \times (h_r - h_p) \tag{1}$$

where Q_r is the stream-aquifer flow (L^3T^{-1}); R_c is the hydraulic conductance of the stream-aquifer interconnection (L^2T^{-1}); h_r is the water elevation of the stream(L); and h_p is the piezometric head in aquifer (L).

Two different directions for stream-aquifer exchange flow are considered for each river cell at each time step: flow from the *aquifer to river* ($Q_{A \to R}$) and flow from *river to aquifer* ($Q_{R \to A}$). The majority of streams in the Seine River network are gaining streams with the net aquifer-to-stream flow values between 0 and +0.1 m^3/s, which means the aquifer system supplies the river network and only few river reaches are losing flow to the aquifer (Pryet et al. 2015). Based on this fact, the assumption was that the transfer of constituent to the aquifer from river is negligible. Therefore, $Q_{A \to R}$ is used in the stream-aquifer solute modeling. Nitrate load transported by aquifer is calculated by multiplying both sides of equation (1) by a nitrate concentration:

$$L_{A \to R} = C_x \times R_C \times (h_r - h_p) \tag{2}$$

where $L_{A \to R}$ is the nitrate load transported by *aquifer to river* flow (MT^{-1}); and C_x is the nitrate concentration (ML^{-3}), which is provided based on the coupling of EauDyssée and STICS.

As a final model outputs of the modeling framework, the in-stream nitrate concentration (with the unit of mg/l) was simulated by the first order decay rate for entire river network. This approach has been extensively applied to study nutrient study at the basin scale (e. g. Liu et al., 2008, Runkel 2007; Smith et al., 1997; Tavakoly et al., 2016a). The decay rate (k) was determined based on the uptake length and the stream velocity:

$$k = \frac{V}{S_w} \qquad (3)$$

where: V is the stream velocity (LT^{-1}) and S_w is the uptake length (L).

Using the RAPID streamflow simulations, time series of the stream velocity for all river cells was computed by the QtoZ module. The range of S_w is defined based on the stream order. Using the predefined range in Table 2 (Ensign and Doyle, 2006), the uptake length is determined for river cells through the calibration procedure. The k coefficient was then calculated for all river cell and time steps.

2-2-4-Limitation of Modeling Framework

In terms of framework limitations, STICS model computes the full nitrogen cycle within the upper soil, and the amount of leaching nitrogen (Brisson et al., 2003). Once leached, only the convection is taken into account, both in the unsaturated and saturated zones, with time transfer varying according to the characteristics of each grid cell. Therefore, there is no nitrification, denitrification nor mineralization once the nitrogen has left the soil column. This is the reason why a decay rate is considered. The decay rate is varied according to the stream order of the river cell, which is explained in the following section. Additionally, the modeling chain include drainage (downward flux in the soil associated to gravity). However, it doesn't include a special treatment for those agricultural area that are drained using artificial pipe, because the data to account for it at the basin scale are not available.

2-2-5-Calibration Process

Calibration of the nitrate concentration in the river network was conducted manually using daily nitrate concentration over the period 1995-2000. The uptake length (S_w) was optimized using three objective functions: Root Mean Square Error (*RMSE*), Correlation Coefficient (ρ), and Kling–Gupta Efficiency (*KGE,* Gupta et al., 2009). The strength of *KGE* is to optimize solution from the three-dimensional criteria space considering correlation, variability, and bias, which is an explicit component in this performance metric (Bennett et al., 2013; Haas et al., 2016). The parameter S_w was adjusted within the defined range in Table 2 by trial and error to obtain maximum ρ and *KGE* and minimum *RMSE*. Once the optimized S_w is obtained, the decay rate (k) was calculated using equation (3). This method allows determination of a temporal variation of k (daily scale), since the velocity varies with time in equation (3). The optimized S_w was then assigned to river cells around each station. Moreover, lower and upper bands, $4x10^{-5}$ and $1x10^{-3}$ (s^{-1}) for k , were contemplated in this study (Faulkner and Campana, 2007; Runkel, 1998). The optimized S_w and temporal averages of k for different stream orders are shown in Table 2.

Table 2: Range of S_w and summary of calibration results for S_w and k.

Stream Order	Range	Mean	
	S_w (m)	S_w (m)	k (s^{-1})
≤ 3	84-996	610	0.000912
4-5	119-1006	930	0.000530
≥ 6	170-4915	1961	0.000270

The magnitude of the obtained S_w and k values in this study is in the same order of published values (S_w = 671 m and k =1.5 x 10^{-3} s^{-1}) by Klocher et al., (2009), which was a study on rivers with stream order less than three.

2-3-Modeling Framework Applied to the Seine River Basin

Following the same methodology as in Beaudoin et al., 2016, the EauDyssée and STICS models were coupled for nitrogen transport simulation in the Seine River Basin for a long-term period (from August 1, 1971, to July 31, 2010). The schematic framework for the spatial coupling of EauDyssée and STICS was displayed in Figure 3. The first step in superimposing EauDyssée was to calculate nitrate flux for each surface cell. GIS was utilized to determine the spatial contribution of nitrate flux to surface cells. The intersect tool in ArcGIS is applied to correlate corresponding GSUs to the surface cells and to compute the areal proportion of the GSU that overlaps with the surface cells. In the second step, nitrate flux (STICS output) was diluted by runoff and infiltration for each surface cell with the assumption of both having the same concentration:

$$C_s = \frac{\varphi_s}{Q_R + Q_I} \tag{4}$$

where C_s and φ_s are the nitrate concentration (ML^{-3}) and nitrate flux (M) at each surface cell; Q_R and Q_I are daily runoff and infiltration (L^3).

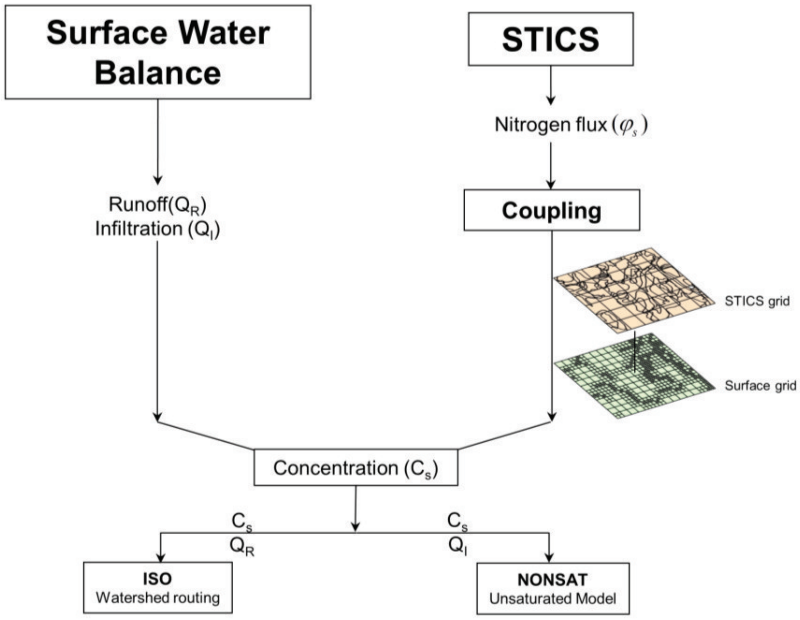


Figure 3: Schematic representation of the spatial coupling of EauDyssée and STICS.

Runoff and infiltration are calculated by the surface water balance component of EauDyssée. Once the nitrate concentration was calculated for all 35,698 surface cells at all time steps in the study period, the solutes were transferred through the unsaturated zone, groundwater and routed by EauDyssée to river cells at a daily time steps. The results for the hydrologic and hydrogeological components of the framework builds on previous results carried out by Philippe et al., (2011), Pryet et al., (2015), Saleh et al., (2011). In their work, the EauDyssée streamflow results were calibrated and validated by comparing simulations to measurements at 118 gages within the Seine River Basin (Pryet et al., 2015). The simulated flows were then used to compute daily nitrate concentration for 6,481 river cell covering the Seine River Basin in this study. Using the first order uptake, the daily nitrate concentration was then computed by routing the mass from upstream to downstream in the river network from 1971 and 2010. Daily riverine nitrate concentration was simulated for 6,481 river grid-cells of which 3,519 interacted with aquifers (Figure 4).

2-3-1-Groundwater initialization

To compare observed and simulated groundwater nitrogen concentrations, special attention was paid to the setting of the initial condition. Indeed, the time transfer in the unsaturated zone can last more than 30 years (Philippe et al., 2011). To set the initial concentration, three periods with different nitrogen leaching concentration were considered with the EauDyssée runs: the first period is pre-industrial (before 1935), and considered that the lixiviated nitrogen can be similar to the one from current organic farming. According to Thieu et al., (2010), a homogeneous concentration of 26mg/L was used. Such forcing data was repeated long enough and the EauDyssée was run to reach a stable groundwater concentration. The results were then comparable to the data collected by Landreau and Roux (1984) in 1930. The second period lasts from 1935 to 1970. For this period, the nitrogen lixiviation was considered to increase linearly between the pre-industrial value and the value estimated by STICS for the period of 1970-1971. For the last period, the nitrogen leaching is estimated by STICS.

2-4-Observation Data

More than 6,000 wells monitoring the groundwater quality in the Seine River Basin are available from the Accès aux Données sur les Eaux Souterraines (ADES) database (http://www.ades.eaufrance.fr/). However, they cover different time periods and are not all available for a given date. Observed river nitrate data were also used to evaluate and compare modeling results. In total, 72 stations with more than 150 sampling dates were available between 1985 and 2010 (Figure 4). The selected water quality stations cover wide range of drainage area,

O(100-10,000) km^2. Five of the water quality stations were selected to discuss comparison between daily time series of observed and simulated streamflow and nitrate concentration. Selected stations are shown with green colored dots in Figure 4. The Poses station, located downstream of Paris before the tidal influence, was used to assess the overall performance of the Seine River Basin model with the drainage area of 64,820 km^2 (Figure 4). The Aronde at Clairoix station is located in the northern part of the Seine River Basin with high agricultural activity. The Torcy station is located on the downstream of the Marne River, an eastern tributary of the Seine River Basin. The Montereau-Fault-Yonne station is on the Seine River which is located downstream of Troyes. The Saint-Aubin-Sur-Yonne station is located on the Yonne River, the southeast tributary of the Seine River.

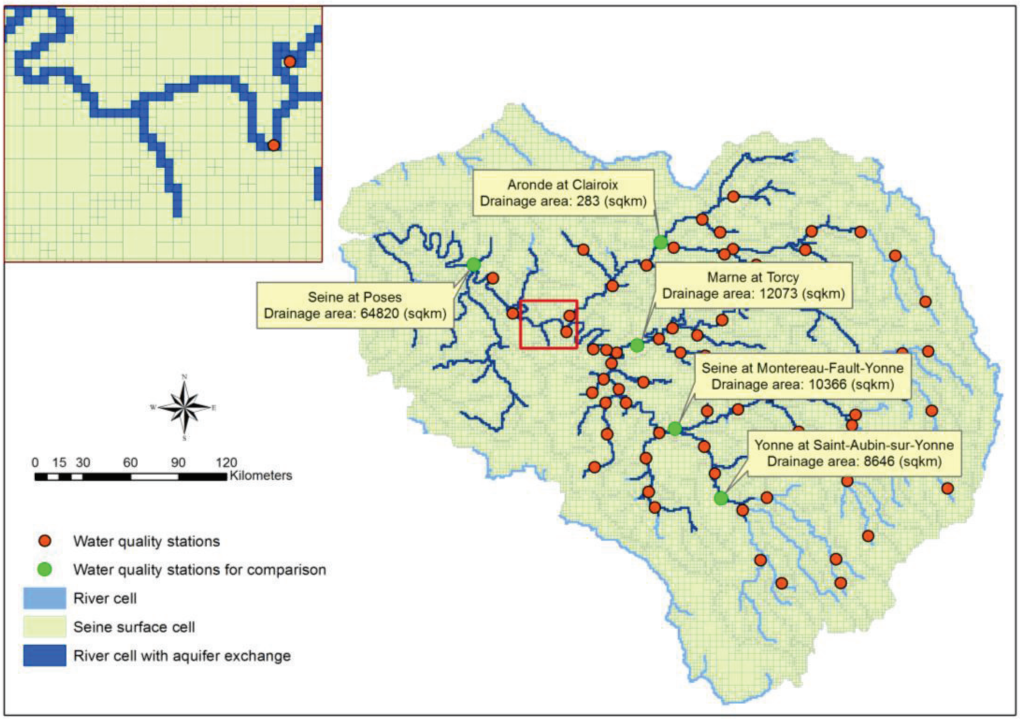


Figure 4: The EauDyssée river network and water quality stations used in this study with their respective drainage areas.

3-Results and Discussion

This section covers three topics: evaluation of the nitrate concentration in groundwater, comparison of the annual inflow and nitrate flux, and evaluation of the in-stream nitrate concentration. The EauDyssée platform was run at a daily time step for the groundwater modeling and at the 30-minute time step for the streamflow modeling to simulate daily nitrate flux over 39 years (1971-2010).

3-1-Comparison of Simulated and Observed Nitrate Flux in Groundwater

Following the method described in the section 2-3-1, the evolution of the groundwater concentration compared quite well with the observations (Figure 5). The map shows that the concentration is above the 50 mg/L target threshold in many parts of the aquifers. Figure 6 presents the mean bias between the observed and simulated concentration during the period 1970-2010 ($\text{Bias} = \overline{C_{\text{simulated}} - C_{\text{observed}}}$). It appears that the absolute bias is less than 10mg/L on average. The large bias (bias > 30 mg/l) was found in the northern tributary of the Seine River (Oise River). This could be explained by the fact that the hydrogeology model is less representative in this part of the Seine River Basin (Pryet et al., 2015). Beaudoin et al., 2016 showed that the overestimation of lixiviated nitrogen could occur in this area due to an underestimation of the yield by the STICS model. Figure 7 presents the temporal evolution of the observed and simulated nitrogen concentration on average on the 3 aquifer layers. The method used to initialize the nitrogen concentration in groundwater is able to provide a nitrate concentration compareble to the observations at the beginning of the simulated period (1970), except for the Oligocene. From 1970 to 2010, the simulation reproduces quite well the increase in nitrate concentration in Chalk, the largest aquifer, underestimates in the Eocene and ends with a concentration close to observations in the Oligocene

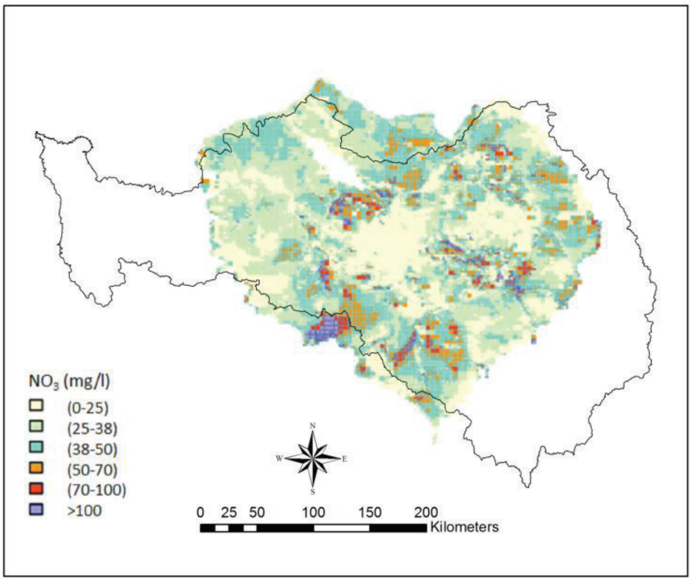


Figure 5: Average concentration of groundwater nitrate in 2010.

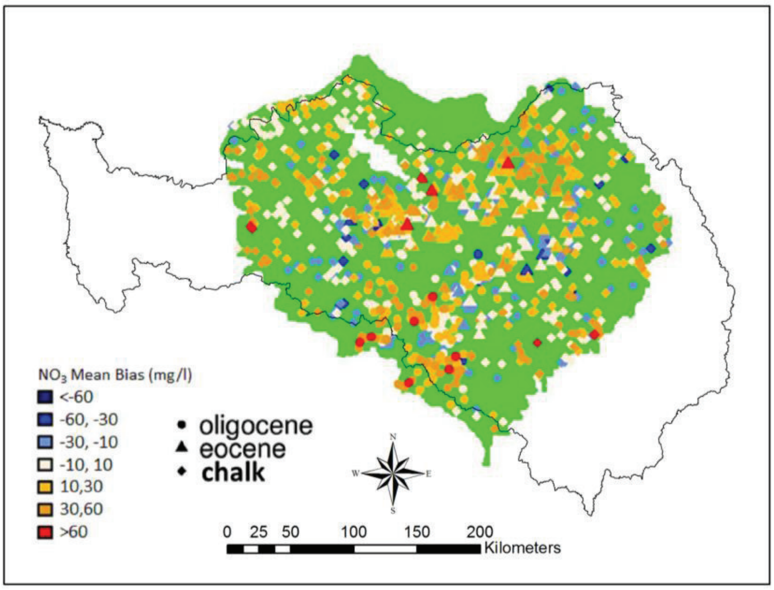


Figure 6: Spatial distribution of the mean bias between observed and simulated nitrate concentration, with the distinction of the 3 aquifer layers (note that the gage can be in a confined part of the aquifer).

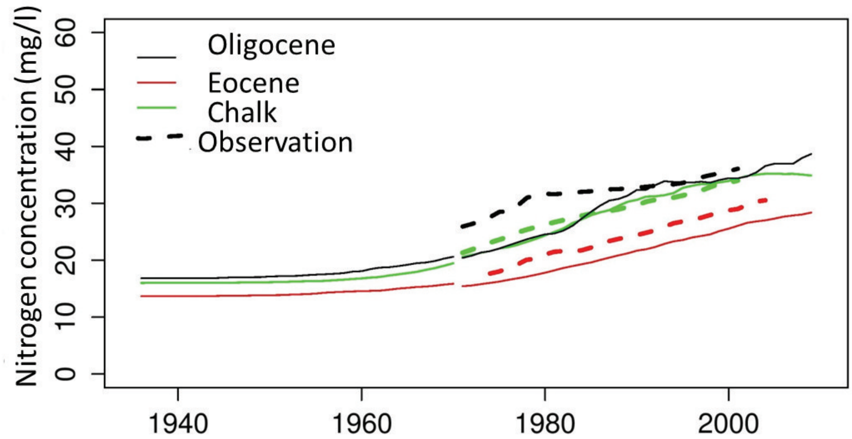


Figure 7 Temporal evolution of the mean observed and simulated nitrogen concentration in the three aquifer layers.

3-2-Comparison of Annual Average for the Simulated Inflow and Nitrate Flux

Nitrate fluxes leaching to rivers are carried by surface runoff and groundwater. To better understand nitrate delivery, the annual average of nitrate flux was compared with annual average of inflow to river cells (Figure 8). Results show that the amount of nitrate delivered to river cells is highly dependent on inflow. The amount of leaching nitrate is low during the dry years, and increases during the wet years, which is consistent with having more leaching in the wet years than the dry years. For example, the lowest amount of nitrate was delivered in 1996 and 1997 at the Poses station, while the annual average of inflow in these years was 173 and 382 m^3/s, respectively. In contrast, in wet years, the annual average is significantly increased. The model outputs show that 2000 and 2001 were characterized by very high discharge rates. The delivered nitrate was also increased for these years. In general, low nitrate load was delivered to rivers in 1976, 1985, 1990-91, 1996, and 2005-06, which were characterized as dry years. On the other hand, high amount of nitrate was delivered to rivers in 1988, 1993, 2000, and 2001. These years had a high discharge and were categorized as wet years. The increasing of nitrate during wet years can be explained by the effect of rainfall. During wet years, the heavy rain causes accumulation of rainfall and raising the water table which will increase the storage of nitrogen in the shallow soil layers and subsequently, more nitrate is transported to rivers. During the dry year, the amount of nitrate inclines to develop, due to the low uptake rate by plants, and it will flow to river network during the following wet years. Unlike other stations, the nitrate load leaching to the river cells failed to follow the inflow variation at the Saint-Aubin-sur-Yonne station (Figure 8). This is likely due to the negligible effect of the groundwater in this area where the nitrate load is primarily the surface load.

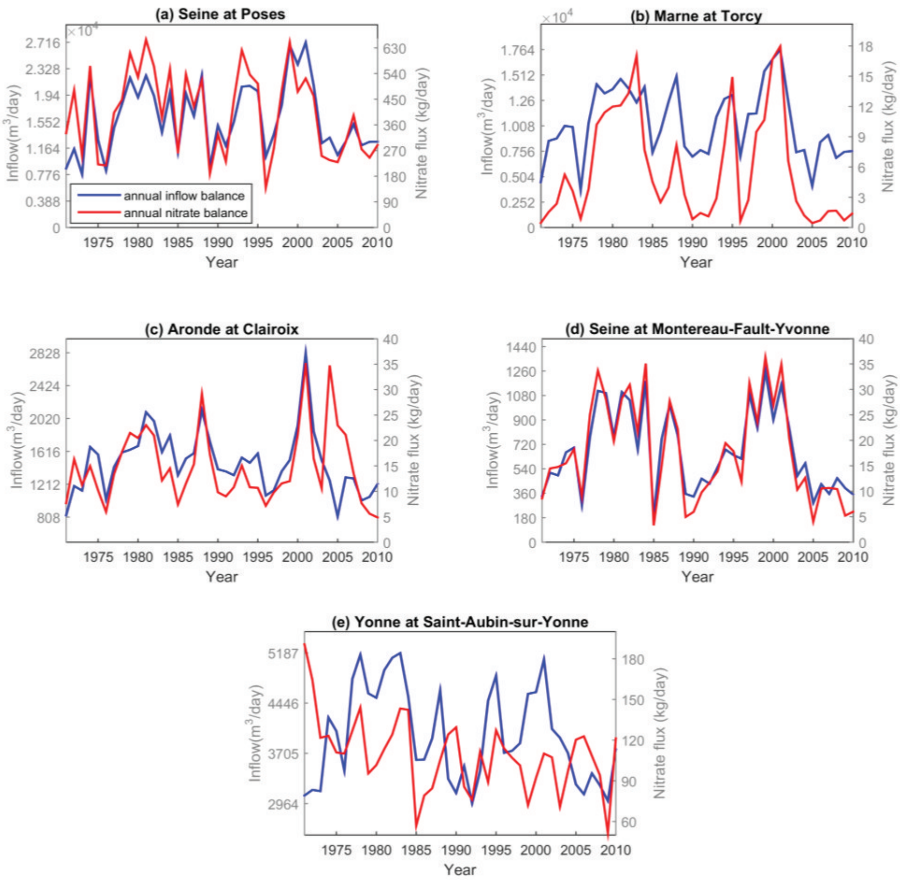


Figure 8: Simulated annual average nitrate flux and inflow for the selected stations: (a) Seine at Poses; (b) Marne at Torcy; (c) Aronde at Clairox; (d) Seine at Montereau-Fault-Yonne; and (e) Yonne at Saint-Aubin-sur-Yonne.

3-3-Simulation of In-stream Nitrate Concentration

Figure 9 shows the KGE values of in-stream nitrate simulations for all stations in this study. The daily *KGE* was calculated using point-by-point concurrently comparison of observed and simulated values. Observed nitrate concentrations are available from 1985 to 2010 for most stations. The spatial distribution of *KGE* values demonstrated an overall satisfactory model performance in terms of simulating long-term daily nitrate concentration. The *KGE* results (Figure 9) indicate that the model performed relatively better in eastern regions of the Seine River Basin compared to the west part of the basin. Clearly, Nitrate concentration strongly depends on the hydrological simulation, which confirms findings from literature (Thieu et al., 2009). A relatively poor performance of EauDyssée with regard to the hydrological simulation in the western part of the basin can explain the reason (Pryet et al., 2015). Additionally, the comparison of nitrate concentration in groundwater (Figure 6) shows relatively large bias in the northwestern tributary of the Seine River Basin (Oise River).

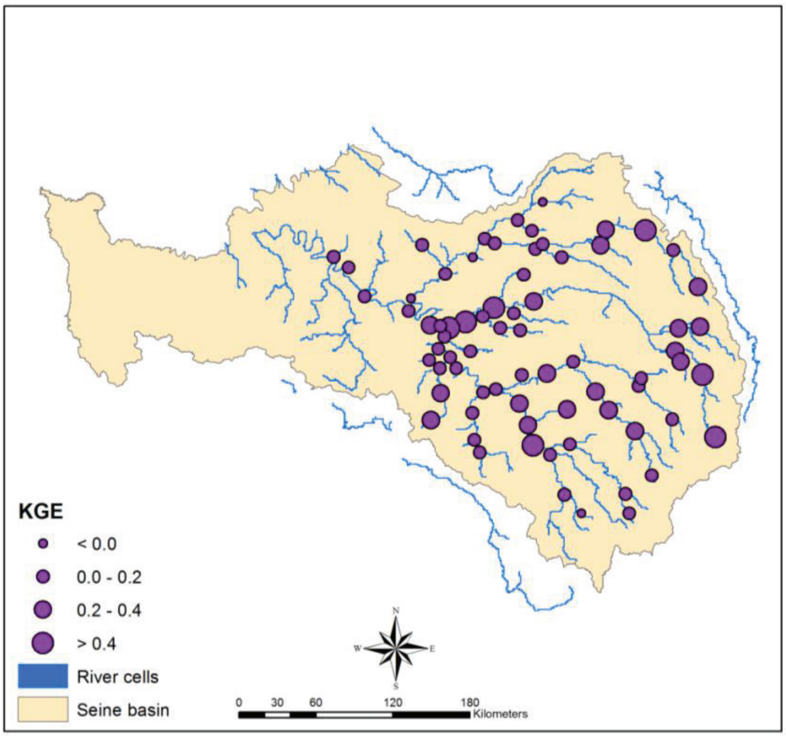


Figure 9: Spatial distribution of *KGE* for all stations using point-by-point concurrent comparison.

Figures 10 and 11 present the comparison between daily observed and simulated nitrate concentrations at the five selected stations between January 1, 1990 and July 31, 2010. The model results illustrate that simulated nitrate concentrations tend to follow the inter-annual variation of observations and hydrographs for the outlet of the basin (the Poses station), Torcy, Montereau-Fault-Yonne, and Saint-Aubin-sur-Yonne. For those stations, the dynamic simulation of the nitrate concentration is consistent with the observation (Figures 10 and 11). More urbanized area can export more nitrate at high flows compared to the low-density suburban area (Klocher et al., 2009). This case can explain high nitrate concentration at the Poses station which is downstream of the greater Paris area. Furthermore, this station is downstream of the Seine River Network with more than fifty percent of agricultural land coverage. The model results for the Poses station in this study are generally in a good agreement with previous studies. The average nitrate concentration for the dry year (1991) and wet year (2001) are obtained 16.5 mg/l (359 µmol/l) and 20.26 mg/l (440 µmol/l). These values are comparable with published results by Sferratore et al., (2005). The annual average of observation and the Riverstrahler model (Ducharne et al., 2007) in 2000 are 22.34 and 35 mg/l respectively for the Pose stations. The mean nitrate concentration of 19.38 mg/l is obtained for the same year in this study. The bias value (Bias = -0.13 mg/l) is also confirmed the slight underestimation of riverine nitrate concentration at this station. The reason is likely due to the point sources loadings to the Seine and Marne Rivers in greater Paris, which were not available for this study.

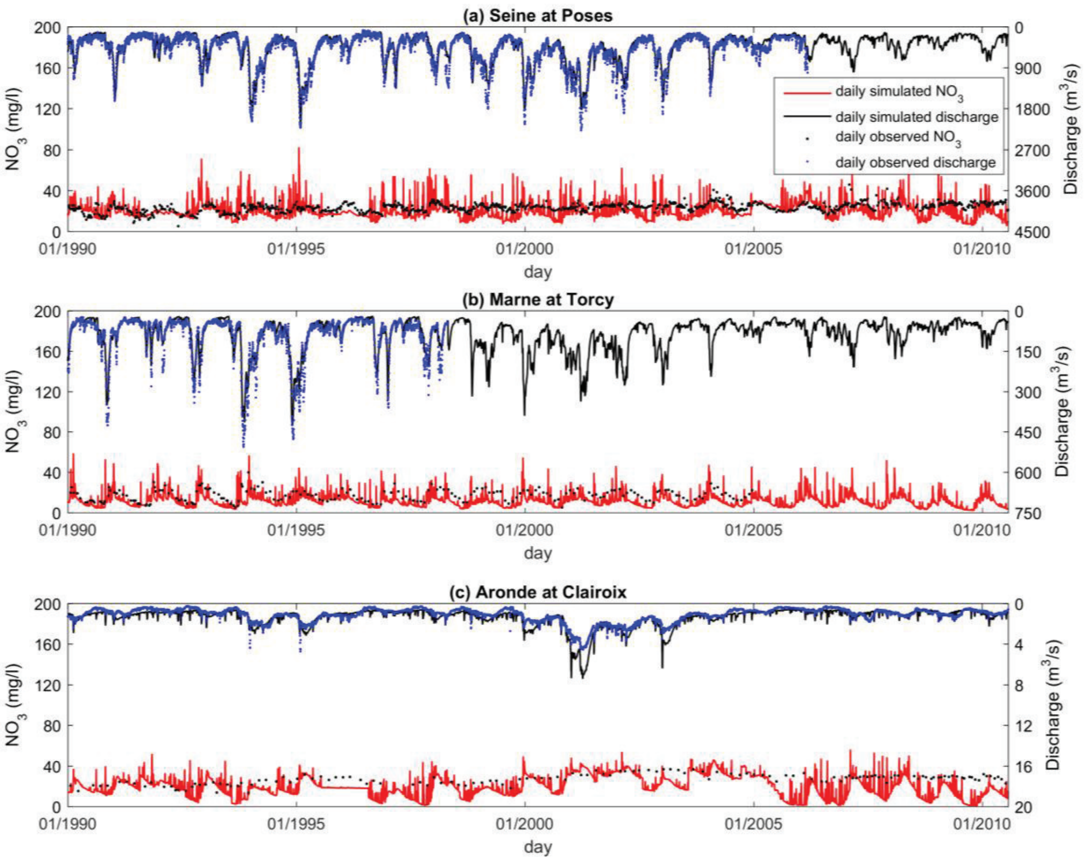


Figure 10: Comparison of daily simulated and observed nitrate concentration and river discharge: (a) Seine at Poses; (b) Marne at Torcy; and (c) Aronde at Clairox. Observed discharge data was not available from March 2006 to July 2010 and from July 1998 to July 2010 for Seine at Poses and Marne at Torcy stations, respectively. Observed nitrate data was not available from January 2006 to July 2010 for the Marne at Torcy station.

Less accurate nitrate simulations are observed at the Aronde at Clairoix station that has a relatively small drainage area of 285 km^2 (*KGE* = 0.13 and correlation = 0.42). For the Clairoix station, the model simulated numerous peaks in 2008 (Figure 9c). The summer of 2008 was quite rainy, which explain such peaks. However, the peaks did not appear in the observations, which might be due to the low frequency of the sample analysis. The nitrate concentrations were measured almost monthly (one or two samples per month). This indicates the need for higher spatial resolution modeling to resolve the complex physics at the local scale of the basin, which is an active subject for future research and continuous observation (based on samples conditioned to the river flow). The nitrate concertation at the Aronde at Clairoix station shows high average values. The upstream region of this station is heavily dominated with cropland, thus the emission of the nitrate to river network from this part of the basin is high. Long-term nitrate simulation at Torcy and Saint-Aubin-sur-Yonne stations were simulated with a good accuracy. For the Torcy station *KGE* = 0.6 and correlation = 0.70 were obtained. Similarly, *KGE* = 0.45 and correlation = 0.60 were calculated at the Saint-Aubin-sur-Yonne station.

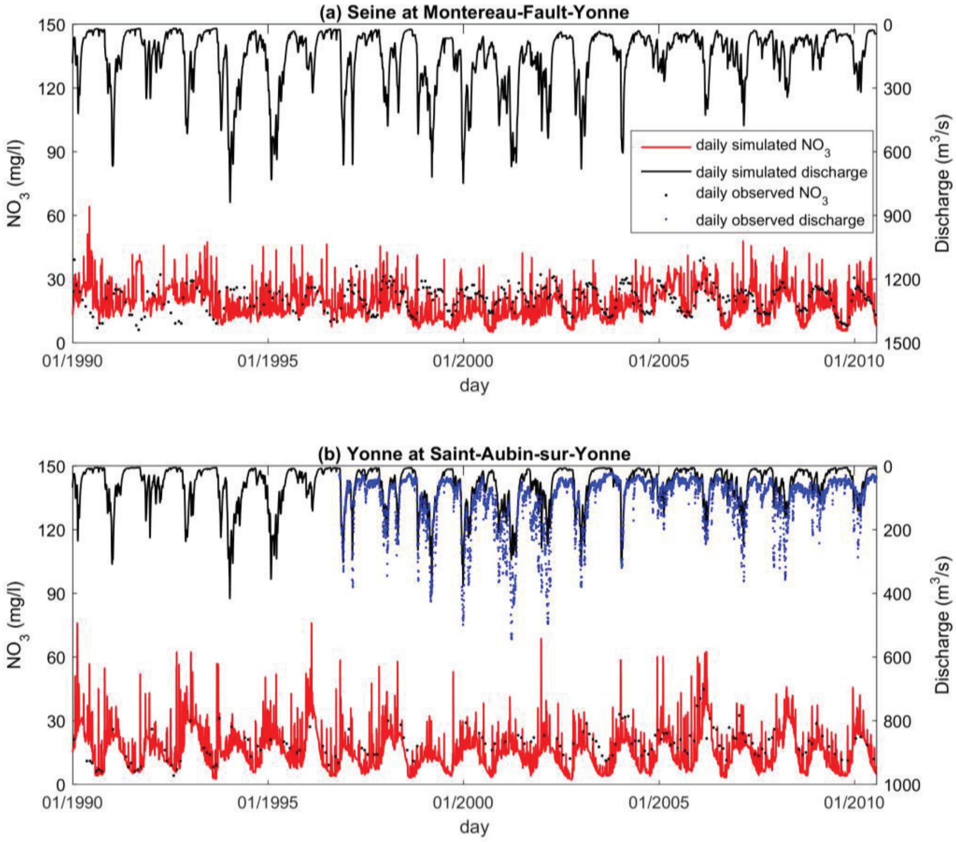


Figure 11: Comparison of daily simulated and observed nitrate concentration and river discharge: (a) Seine at Montereau-Fault-Yonne; and (b) Yonne at Saint-Aubin-Sur-Yonne. Observed discharge data was not available for the Seine at Montereau-Fault-Yonne for study time period. Observed nitrate data was not available from January 1990 to October 1996 for the Yonne at Saint-Aubin-sur-Yonne station.

Changes in the nitrate concentration are highly affected by the hydrologic simulations. To have a better representation of variation in nitrate and flow simulations, the seasonal simulations are also calculated. For this purpose, the daily model results were averaged monthly and the seasonal comparison was conducted (Figures 12 and 13). A general trend between riverine and flow simulations can be clearly seen in these figures. Results show that the model captured most of the seasonal variation of nitrate concentration. Major underestimations of the simulated nitrate are found during dry season (summer). Such an underestimated simulation is likely due to the complexity of nitrate attenuation pathways in the groundwater. The discrepancy between observation and simulation can be seen at the the Aronde at Clairoix station. As mentioned before, this station has less frequent measurements compare to other stations and higher resolution model for this part of the basin could provide more details.

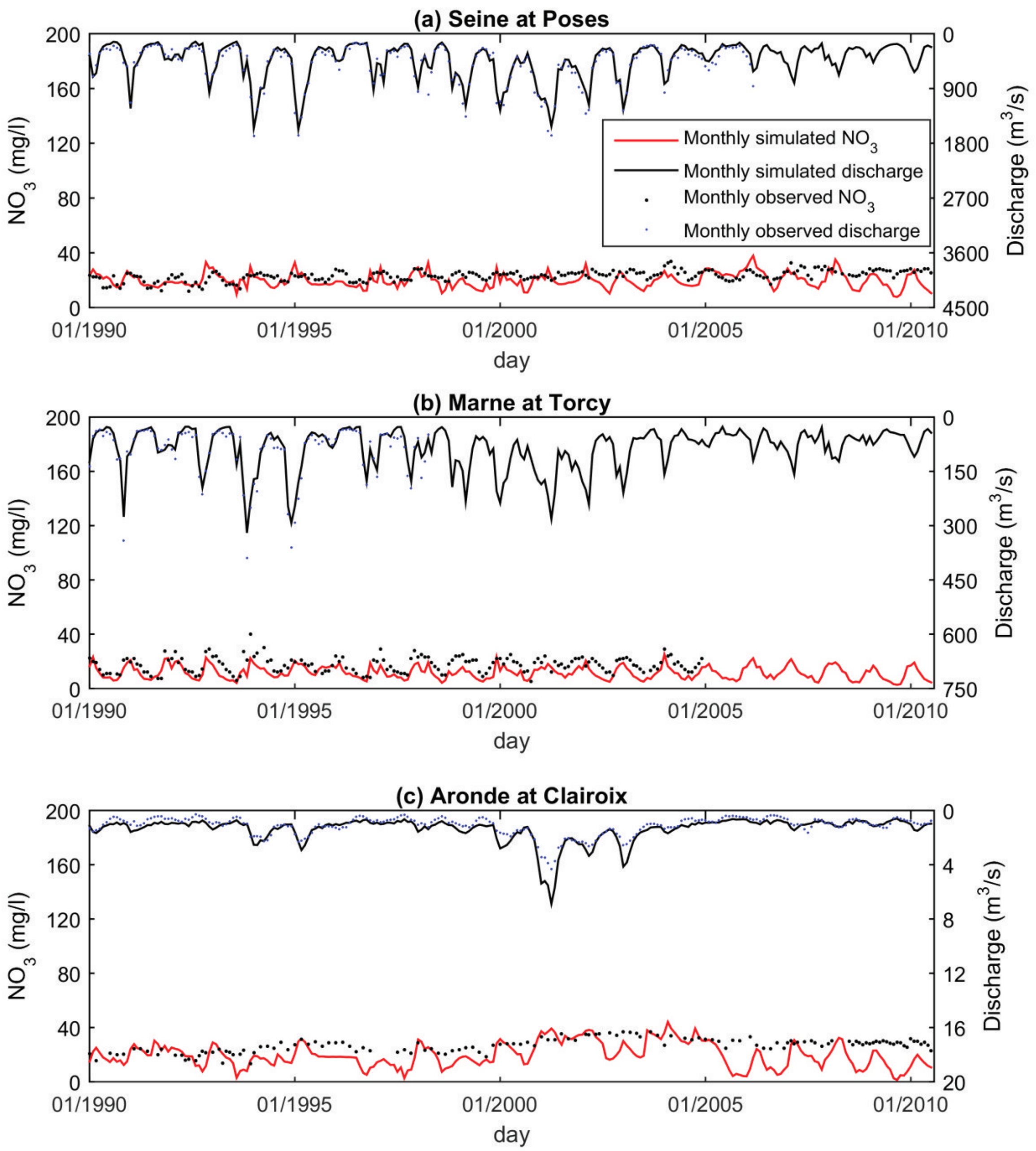


Figure 12: Seasonal comparison of simulated and observed nitrate concentration and river discharge: (a) Seine at Poses; (b) Marne at Torcy; and (c) Aronde at Clairox.

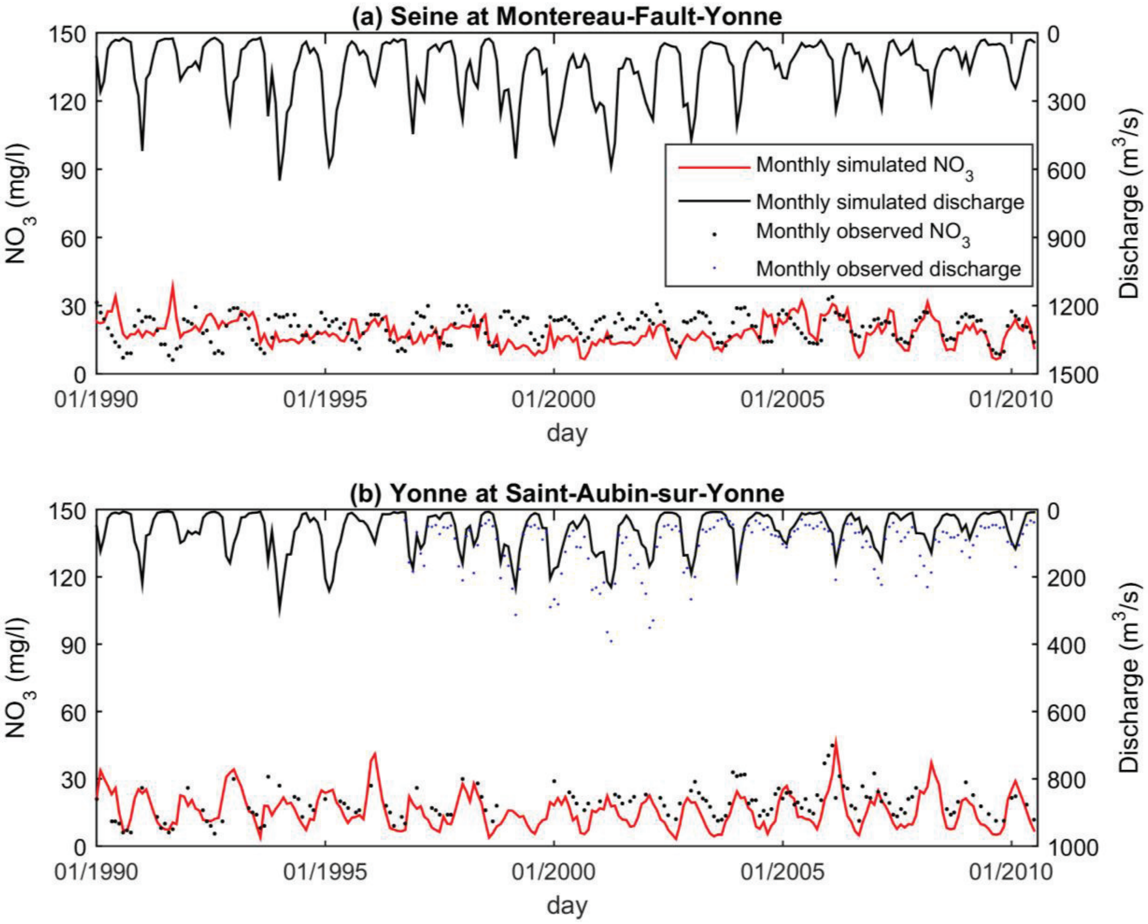


Figure 13: Seasonal comparison of simulated and observed nitrate concentration and simulated river discharge: (a) Seine at Montereau-Fault-Yonne; and (b) Yonne at Saint-Aubin-Sur-Yonne.

Figure 14 displays the spatial distribution of riverine nitrate concentration in 1990 (dry year) and 2001 (wet year). From this figure, the change in nitrate concentration can be qualitatively assessed for each river cell, which may provide useful information for the regional-scale nitrate management. For example, comparison of the simulate nitrate concentration between 1990 and 2001 show that nitrate concentration increases in the south part of the Seine River Basin (Loing River). The maximum annual nitrate concentration also displays approximately 60% difference (an increase) comparing a wet year (2001) and a dry year (1990). Different in-stream nitrate concentration for these years is largely driven by differences in river water discharge. Annual water yield in 2001 was roughly double as much as in 1990.

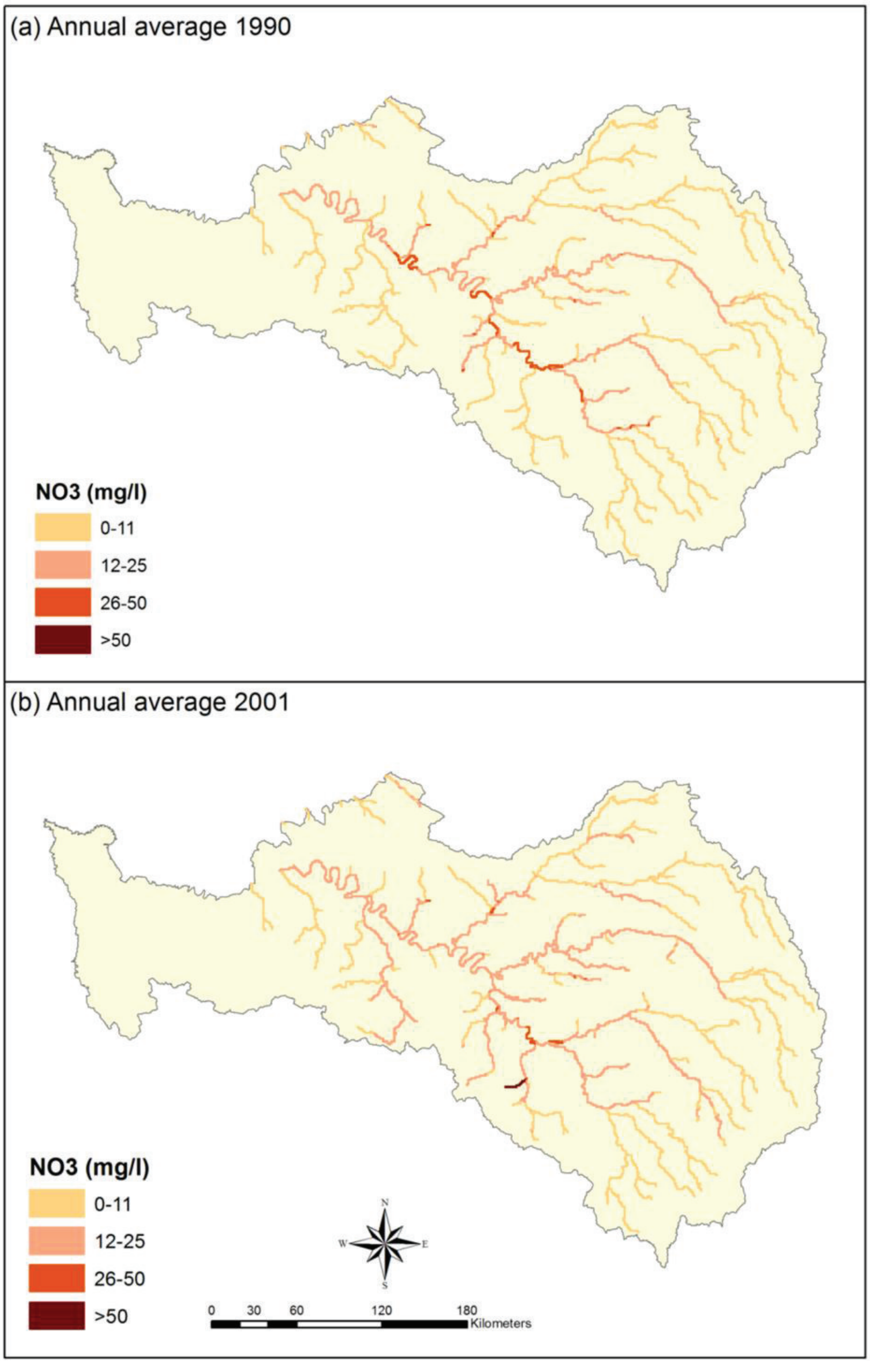


Figure 14: Spatial variation in nitrate concentration for the Seine River Basin in (a) 1990 and (b) 2001.

4-Summary and Perspective

This study describes the implementation of coupled EauDyssée and STICS models to the entire Seine River Basin with total area of 88,000 km^2. The EauDyssée modeling platform was enhanced to simulate long-term (1971-2010) daily nitrate transport in addition to water transport from surface to rivers and aquifers. The surface and river interactions with aquifers were also considered for the nitrate transport process. The hydraulic variables of river cells such as river flow velocity were computed for the entire basin for the study period. Using the EauDyssée hydrological results, the first order solute transport was developed to simulate riverine nitrate concentration. The spatiotemporal variation of the decay rate was calculated based on the stream order and daily river velocity for river cells. The in-stream nitrate concentration was then simulated for the grid river network (6,481 river cells), which is the backbone of the river routing module of EauDyssée. The simulated in-stream nitrate concentration was calibrated with observations for the selected stations. Simulated groundwater nitrate concentration is comparable to the observation with a bias lower than 10 mg/l in most part of the basin. Comparison of nitrate flux and inflow showed that simulated nitrate is highly dependent on the inflow produced by surface and subsurface waters. Variation of mean annual nitrate from year to year can be explained by the hydrologic regime of that year. Large amount of nitrate flux transports during wet years and less transports during dry years. The long-term simulated nitrate concentration compares favorably to the measured data on a daily basis, especially in the eastern part of the Seine River Basin.

The EauDyssée platform has been used by stakeholders and decision makers for more than 30 years since its initial MODCOU implementation by Ledoux et al. (1984). The robustness of the EauDyssée platform to simulate complex hydrologic systems with representation of the stream-aquifer exchanges supports the success of the solute transport modeling with the first order approach for riverine nitrate simulation. Hence, this study offers enhanced capabilities for better quantifying water resources and environmental management of Seine River Basin. Long-term computation of flow and nitrate flux may provide a basin-wide comprehensive hydrology and water quality system to study the integration of climate and land surface models with the consideration of rive-aquifer interaction. The outcomes of this study are a good basis for answering needed scientific questions. For instance, this work can provide important perspectives for decision makers focused on the effects of Agri-environment measures and the integration of environmental impacts into the common agricultural policies (Baylis et al., 2008). In addition, this work demonstrates a feasible methodology to quantify the overall variability of the nitrate fluxes in a regional basin stressed by agricultural activities. Furthermore, this coupled framework can be used to project long term climate change effects on nitrate leaching over large-scale basins and to provide stakeholders with tools that quantify the long-term loads and concentration of nitrate (Dirnböck et al., 2016).

This study focused on the non-point source pollution and did not include point source pollution sources such as waste water treatment because of data non-availability. Including such data in the modeling framework can improve the estimation of nitrate and the overall bias. Future work can address uncertainty from input data (Thorsen et al., 2001) and model structure using stochastic–deterministic approaches or generalized likelihood uncertainty estimation (GLUE) methodologies (Beven and Binley, 1992).

The modeling framework in this study has the flexibility to add or remove nitrate constituents without excessive programming effort. Due to the modeling features and capabilities of the framework presented in this study, this framework can be applied over other basins for water resources and contaminant studies. It offers important perspectives for future large scale applications coupled with existing hydrologic models such as the Soil and Water Assessment Tool (SWAT) (Abbaspour et al., 2015) and the Weather Research and Forecasting-Hydrological (WRF-Hydro) modeling system (Gochis et al, 2015).

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