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Keywords

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Abstract

Denitrification in riparian wetlands plays a major role in eliminating nitrate coming from agricultural watershed uplands before they reach river water. A new approach was developed for representing this process in the biogeochemical Riverstrahler model, using a single adjustable parameter representing the potential denitrification rate of wetland soils. Applied to the case of three watersheds with contrasting size, land-use and hydro-climatic regime, namely the Seine and the Loir rivers (France) and the Red River (Vietnam), this new model is able to capture the general level of nitrate concentrations as well as their seasonal variations everywhere over the drainage network. The nitrogen budgets calculated from the results show that riparian denitrification eliminates between 10 and 50% of the diffuse sources of nitrogen into the hydrosystem coming from soil nitrate leaching.

Acknowledgements

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Introduction

The Nitrogen Cascade (Galloway et al., 2003) designates the chain of transfers, transformations and effects initiated by the release into the environment of reactive nitrogen forms from agriculture and other anthropogenic activities (Sutton et al., 2011). In areas with intensive industrial agriculture, nitrate contamination of ground- and surface water is widespread and a major threat for drinking water resources, aquatic biodiversity and coastal water ecosystem health (Grizzetti et al., 2011; Billen et al., 2011).

Much debate exists regarding the level of nitrate concentration in surface river water that can be considered desirable. For drinking water, the maximum threshold set by the World Health Organization (WHO) (1970, reconfirmed in 2007) is 10 mgN/l, very close to level recommended by the European Drinking Water Directive (EC 98/83, 1998): 11.3 mgN/l (50 $mgNO_3$/l). Half this value (5 mgN/l or 25–30 $mgNO_3$/l) is often stated as a groundwater objective or vigilance level (AESN-SDAGE http://www.eau-seine-normandie.fr/mediatheque/flipbook_sdage/index.html). In surface water, a strong decrease in hydrophyte biodiversity is observed above a nitrate concentration of 2 mgN/l (James et al., 2005). This is also the level recommended by Camargo et al. (2005) for protecting the most sensitive freshwater species. As far as freshwater eutrophication risks are concerned, total N concentration levels above 1.5 mgN/l are considered to be a potential risk (Grizzetti et al., 2011). For coastal marine eutrophication, because the problem is linked to excess nitrogen over silica with respect to the needs of diatom growth (Billen & Garnier, 2007), the maximum nitrate threshold should be related to the river silica concentration. As the latter varies within the range 3–7 mgSi/l under a temperate climate (Garnier et al., 2006), the corresponding maximum nitrate concentration must be within the range 1.2–2.8 mgN/l. Clearly, the water quality objectives for river water should be much lower than those stated for groundwater.

Nitrate concentrations in temperate European rivers are frequently 25–50% lower than in the groundwater feeding them (Billen & Garnier, 2000; Passy et al. 2013). They also often show seasonal variations with lower values in summer low-water than in winter high-water periods. This can in some cases be related to a larger contribution to total runoff of groundwater baseflow (if they have a lower nitrate concentration than surface runoff) in summer than in winter (Thieu et al., 2009). The seasonality of the river nitrate concentration has also been attributed to denitrification in riparian wetlands, more active at high summer temperatures.

The latter conclusion is supported by strong isotopic evidence, because the low nitrate concentration in summer low water is associated with the clear ^{15}N signature of a riparian denitrification process, and cannot be the result of in-stream denitrification by benthic processes (Sebilo et al., 2003). Direct measurements of nitrate concentration along topographical gradients from the agricultural plateau down to river banks (Cey et al., 1998; Hill et al., 2000; Devito et al., 2000; Ranalli & Maclady, 2010) clearly illustrate the role of riparian denitrification. In situ measurements of denitrification rates also show that riparian wetlands, together with areas where water tables remain shallow for extended periods (Burt et al., 1999; Clement et al., 2002; Anderson et al., 2014; Oeler et al., 2008) are hotspots of denitrification in the landscape. Yet, modeling this process at the watershed scale remains a difficult task.

At the landscape scale, models like Nitroscape, TNT2 and CASIMOD'N (Salmon-Monviola et al., 2012; Duretz et al., 2011; Moreau et al., 2013), based on a comprehensive description of all processes of water and nitrogen transfer and transformation, calculate at a metric grid scale all processes of the nitrogen cycle, including denitrification, plant uptake and storage in the soil organic matter pool. Such models allow one to estimate "landscape nitrogen retention" at a very fine spatial resolution. The application of such a fully spatially distributed modeling approach is limited, however, to landscapes smaller than a few dozen square kilometers.

At the other extreme, the NANI approach (Howarth et al., 1996), designed for application at the scale of large watersheds, reduces all processes related to the N cascade to a black box with inputs (fertilizer application, atmospheric deposition, symbiotic N_2 fixation, net imports of N in agricultural commodities) and output (river N flux at the watershed outlet). The balance defines a "N retention" term, typically 40–80% of the inputs, which can be empirically related to temperature and specific discharge (Howarth et al., 1996, 2006; Billen et al, 2010, 2005, 2006), without, however, providing any clues on the nature of the processes involved. The term "retention," although commonly accepted in the literature, is misleading because only a fraction of the "missing" N is indeed stored in the landscape, the rest being denitrified to the atmospheric nonreactive N_2 pool, with, however, a fraction emitted as N_2O, a powerful greenhouse gas (Garnier et al., 2014).

Models such as Sparrow (Alexander et al., 2001; Smith et al., 2007), Green (Grizzetti et al., 2005, 2006) and Nutting-N (Dupas et al., 2013; 2015) are a little more explanatory. Among retention processes they distinguish between those occurring in the terrestrial part of the basin (and acting on diffuse sources of nitrogen) and those occurring in the river network (acting on both diffuse and point sources of nitrogen). Both retention types are parameterized according to hydrological and landscape characteristics of the watershed and calibrated on the basis of multiannual averages of observed nitrogen load at the outlet of the watersheds. These models generally show the predominance of terrestrial versus in-stream retention processes.

The SWAT (Neitsch et al., 2005) and Seneque-Riverstrahler (Billen et al., 2000; Ruelland et al., 2007) models are both based on a spatially distributed representation of the river network, a seasonal temporal resolution and a mechanistic description of in-stream processes. Both models are fed by a 0D semi-distributed model of nitrogen transfer in the watershed's agricultural soils, based on the hypothesis of additivity of the contribution of each land-use class of the terrestrial watershed. They are therefore intermediate, in terms of spatial resolution and explanatory power, between landscape models and approaches of the Nutting-N or NANI type. However, their weak point lies in the representation of riparian denitrification (Grizzetti et al., 2015). Special modules have recently been developed for a better representation of alluvial denitrification by the SWAT model (Sun et al., 2016). In the Riverstrahler model, riparian retention was initially parameterized as a constant fraction of the nitrate flux transmitted from the watershed (Billen & Garnier, 2000), possibly adjusted on the basis of a typology of river corridors (Curie et al., 2007).

In this paper, we describe a different vision of riparian denitrification based on a more mechanistic description of the processes involved in the interaction of surface and groundwater runoff with riparian wetland soils. We aimed at a better simulation of the spatial and temporal variations of nitrate concentrations in rivers than previous versions of the Riverstrahler model, for both small (100–1000 km²) and large (over 10,000 km²) watersheds.

Methods

1. The Riverstrahler model

The general principles and parameterization of the Riverstahler model have been fully described in the papers by Billen et al. (1994, 2000) and Garnier et al. (2002, 2005). Here we used the Seneque-Riverstrahler version with its GIS interface described by Ruelland et al. (2007) and extensively applied to the Seine, Somme and Scheldt watersheds (Thieu at al., 2009; Passy et al., 2013), as well as to several other watersheds with quite different climate and hydrological regimes and watershed sizes, such as the Lot (South of France) (Garnier et al., 2018), the Red River (China and Vietnam) (Le et al., 2010), the Kalix and Lule Rivers (Sweden) (Sferratore et al., 2008) and the Danube River (Garnier et al. (2002).

A complete description of the biogeochemical RIVE model, which constitutes the core of the Riverstrahler model, as well as a detailed description of the Seneque-Riverstrahler software, is available at www.fire.upmc.fr/rive

Seneque calculates the discharge of each stream of the river network from the superficial and baseflow components of the runoff over its watershed, which have to be specified as an input to the model. They can be obtained either from observed daily discharge data at key stations in the river network using conventional recursive filters (Arnold et al., 1995, 1999; Eckardt, 2005, 2008) or from the results of rainfall-discharge models if they are available on the watershed. In the Riverstrahler model, the absolute values and the relative importance of each of these components vary at each 10-day period, but the chemical composition of each component of the discharge (in particular for nitrate) is considered to remain constant. As explained below, the nitrate concentration in sub-root water flows is calculated from the long term N surplus, leaching and water runoff. The mass conservation between N soil balance and leaching is therefore met on the long run. At the scale of 10-day periods, it is assumed that the magnitude of the N soil pools act as an efficient buffer of nitrate concentration in runoff water in spite of the water flow variations. The N fluxes associated to the superficial and groundwater runoff define the diffuse sources from the watershed, which must be determined as an input to the model for each land use class considered.

For the superficial or hypodermic component of runoff, the nitrate concentration is that of the sub-root infiltration concentration. Depending on the scale at which the model is applied, the land-use classes can simply refer to divisions such as Corine Land Cover classes level 1 or 2 (Ministère de l'Environnement, de l'Energie et de la Mer, 2012), distinguishing urban area, forest and semi-natural areas, grassland and arable land, or they can distinguish many more classes of arable land with, e.g., different crop rotations. In both cases, the nitrate concentration in infiltrating sub-root water is calculated from the nitrogen soil balance (or surplus, kgN/ha/yr), taking into account inputs through fertilizers, manure, symbiotic fixation, atmospheric deposition, and export through harvest in each land use class considered. In the former case, the data are provided by regional agricultural statistics; in the latter case, detailed inquiry regarding the cultural practices and yield are used. The procedure for estimating leaching nitrate concentration from the N soil balance is explained below.

Regarding the nitrate concentration in baseflow, the same concentration as in sub-root fluxes is also considered in the present study, assuming that groundwater has reached its equilibrium with respect to this infiltration concentration. However, another value could be assigned to base-flow, when groundwater nitrate concentration differs from the sub-root one. This can happen for two reasons: either because of the legacy of a previous higher or lower contamination in recharge water in long residence time aquifers (Thieu et al., 2009), or, in some cases, because of a process of denitrification occurring in deep groundwater due to anoxic conditions created by the presence of iron sulfides or residual organic matter (Rivett et al., 2008).

The model simulations in terms of nitrate concentration are compared with the observations available at some monitored stations in the river network. The root mean square error of the model simulation with respect to these observations, normalized to the range of the observations at all stations in the watershed, is used as an indicator of the model's goodness of fit.

2. Modeled watersheds and determination of leaching nitrate concentration

The new version of the Riverstrahler model has been applied in this paper to three different watersheds, with contrasting characteristics, to which the previous version of the Riverstrahler model has already been implemented and published (Table 1). The first one is the Haut Loir River, a 3590-km² tributary of the temperate oceanic Loire River system (Moatar & Dupont, 2016), located in the intensively cropped area of the central Paris basin (www.sage-loir.fr). This area is subjected to high nitrate contamination of ground- and surface water due to intensive cereal cropping and rather low infiltration depth. The second application targets the Seine-Normandy watersheds (94 675 km²) as a whole. The characteristics of this basin, as well as previous applications of the model, are described in detail in Meybeck et al. (1998) and Billen et al. (2007). Finally we present application of the model to the Red River, a sub-tropical river system covering 141 120 km², with a quite different land use, climate and hydrological regime (Le et al., 2010; 2014).

Table 1. *General characteristics of the Seine, Haut Loir and Red River watersheds*

	Haut Loir	Seine-Normandy	Red River
Watershed area, km²	3 590	94675	141120
Active wetland areas, km²	108	5600	30070
Hydrological regime	Temperate oceanic		Subtropical
Mean specific discharge, L/s/km²	3.15	6.17	24.3
% tile drainage	23%	11%	0
% cropland area	68%	50%	44%
Population density, inhab/km²	25	195	158

For these three applications, the procedure for estimating the nitrate leaching concentration from agricultural land differs significantly, because of the different data availability at these different scales. For the Haut Loir watershed, detailed knowledge of the crop distribution and succession is available from the analysis of the graphical land parcel registration declaration for farmers within the scope of the allocation of EU Common Agricultural Policy subsidies (https://www.data.gouv.fr/fr/datasets/registre-parcellaire-graphique-rpg-contours-des-ilots-culturaux-et-leur-groupe-de-cultures-majoritaire/), making it possible to propose a spatialized typology of crop rotations. The corresponding farming practices are also documented for the central Paris basin, based on the data collected and assembled by Puech et al. (2015) and Anglade et al. (2015). From this, an average N soil balance can be calculated for each crop rotation type. At the scale of the Seine watershed, the N soil balance of crop- and grassland is calculated from regional agricultural statistics at the department (Nuts 3) level according to the procedure described in detail by Le Noë et al. (2017). For the Red River basin, a similar analysis was carried out at the scale of the three major sub-basins by Le et al. (2015), combining national and regional agricultural statistics.

To calculate the nitrate concentration from the N soil balance, the following assumptions are considered: (i) Leaching is the major fate (70–80%) of the N soil balance (SoilNbal, kgN/ha/yr), except when catch crops are systematically sown before spring crops or in the case of permanent land cover (Billen et al., 2013; Anglade, 2015; Anglade et al., 2017); (2) The nitrate leaching concentration corresponds to the “dilution” of the annual N leaching flux by the average annual infiltrating water depth (Infiltr, mm/y) and is assumed not to vary seasonally, because of the buffer capacity of soil N pools. The nitrate concentration in leaching water (NO_3, mgN/L) is thus calculated for each land use class as:

$$NO_3 = ICA * SoilNbal / Infilr * 100 \qquad (1)$$

where ICA is an indicator of vegetal soil coverage during high water periods (Anglade et al., 2017).

The results for the three basins are shown in Figure 1.

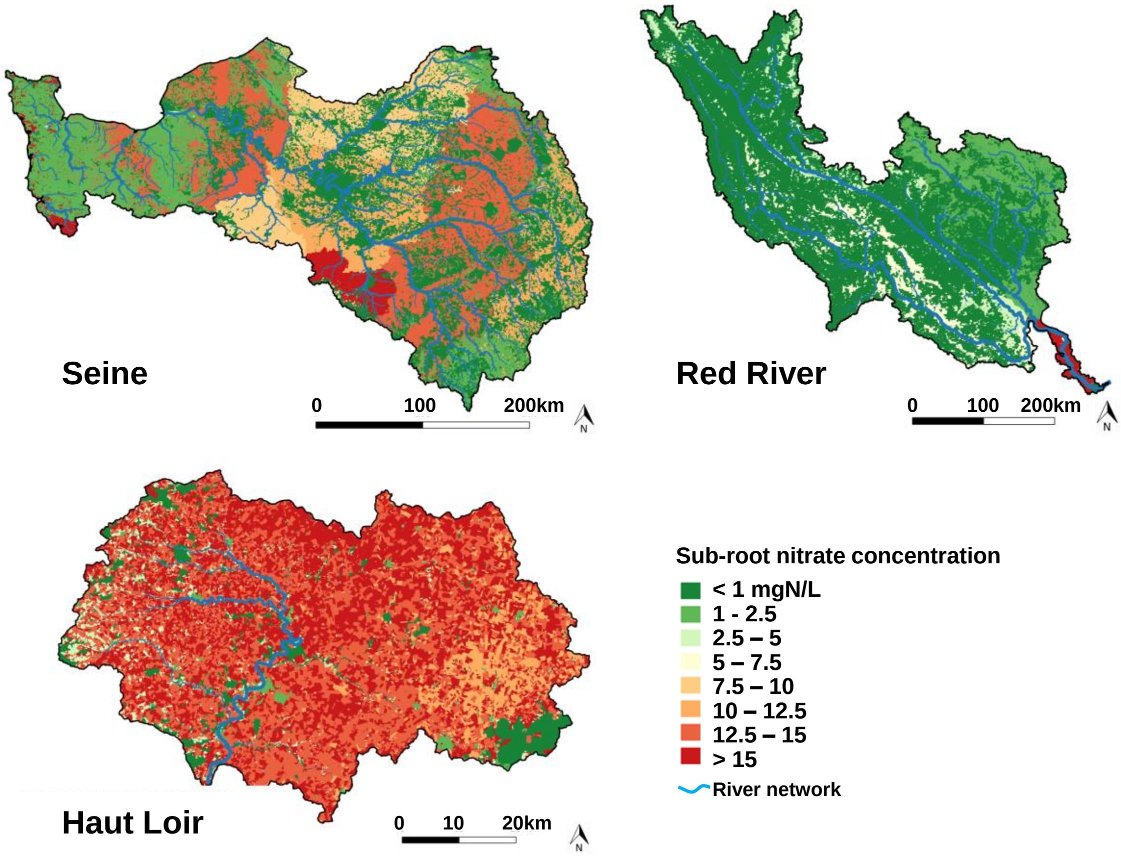

Figure 1. *Distribution of sub-root water nitrate concentrations calculated for the Haut Loir River, the Seine River and the Red River, based on data on land cover and agricultural practices.*

New model developments

1. Conceptual representation of riparian denitrification

The essence of the new representation of riparian retention is illustrated in Figure 2. Before they reach the river bed, superficial and phreatic water flows coming from the watershed, with their nitrate concentration determined by land use and agricultural practices, have to cross a more or less extended riparian area where biogeochemically active superficial soils, often rich in organic matter, are in contact with the river water table. These soils have a certain denitrification capacity (DenCap, gN/km²/h). The relative importance of this capacity with respect to the amount of nitrate crossing the riparian area (NO3Flw, gN/km²/h = SF + BF, see Fig 2) is assumed to determine the extent of the retention per unit watershed area (RR, gN/km²/h).

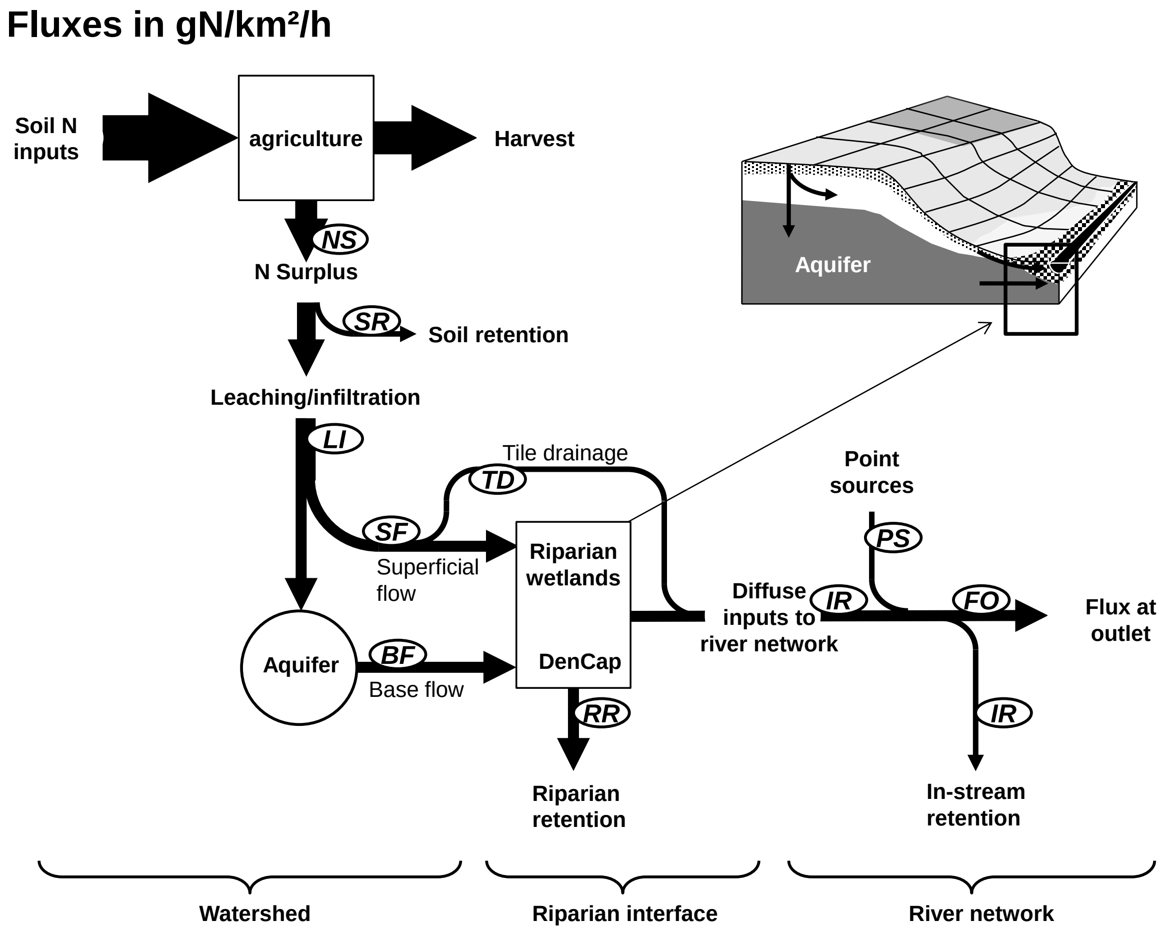

Figure 2. *Processes involved in nitrate transfer from the watershed to surface water as represented in the new module of the Riverstrahler model.*

The riparian denitrification capacity per unit watershed area (DenCap, gN/km²/h) can be expressed as the product of the volume of active riparian wetland soil by the potential denitrification rate per unit soil volume at the current temperature:

$$DenCap = wtld \times depth \times denpot20°C \times tempfct \quad (2)$$

where wtld (m²/km²) is the area of active wetland per unit watershed area; depth is the average active depth where denitrification is concentrated (a value of 0.3 m will be assumed here); denpot20°C is the denitrification potential of the wetland soil at 20°C temperature (in gN/m^3/h) and tempfct represents the effect of temperature on soil denitrification (dimensionless).

The flow of nitrate from the watershed per unit watershed area (gN/km²/h) (SF+BF, Fig 2) is expressed as:

$$NO3Flw = ssr \times NO3m + bfl \times NO3m \qquad (3)$$

where ssr and bfl (m^3/h/km²) are respectively the specific surface runoff and baseflow from this portion of the watershed, NO3m (in gN/m^3, or mgN/L) is the weighted mean nitrate concentration in sub-root water from all land use classes of this portion of the watershed. (Note that we here used the same sub-root concentration for superficial runoff and base flow, assuming groundwater is at equilibrium with the infiltrating water. If documented, another value for baseflow nitrate concentration could be considered as mentioned above).

The flow of nitrate effectively reaching the river (IR, Fig 2) is then given, at each time step, as the difference between the total flow of nitrate coming from the watershed (NO3Flw) and the denitrification capacity of the riparian wetland (DenCap), considering however a minimum threshold (thresh) corresponding to a nitrate concentration of 0.5 mgN/L in the total runoff (see below for a justification of this concentration value):

$$IR = MAX\,(NO3Flw - DenCap, thresh) \qquad (4)$$

$$RR = NO3Flw - IR \qquad (5)$$

When a portion (tl) of the watershed area is equipped with tile drains, the concerned nitrate flow in superficial water (TD) is considered to by-pass the denitrification zone and is not subject to the above calculations. Equations (3) and (4) above become:

$$NO3Flw = ssr\,(1-tl) \times NO3m + bfl \times NO3m \qquad (3')$$

$$IR = TD + MAX\,(NO3Flw - DenCap, thresh) \qquad (4')$$

2. Extent of active riparian wetlands and tile drainage

The soil topographic index (TI), defined by Beven and Kirby (1979), is a useful indicator to estimate the position and extension of wetlands within large watersheds (Mérot et al., 1995; Curie et al., 2007). It is defined for any grid cell of a digital elevation model of the watershed as the natural logarithm of the ratio between the drainage area per unit contour length and the tangent of local slope:

TI = ln [drainage area/ tg(slope)]

TI expresses the propensity of water accumulation according to the topography of the watershed. Curie et al. (2007) have shown that above a threshold of 12.5 (for a DEM of 50×50-m grid), the conditions for hydromorphic conditions are met.

For the whole of France, this approach has been adopted and compared to direct data on soil hydromorphy to provide a national map of potential wetlands (INRA Infosol - AgroCampus Ouest, 2010). (Berthier et al., 2013; http://geowww.agrocampus-ouest.fr/web/?p=1538)

By combining this GIS layer with the Corine Land Cover map (Ministère de l'Environnement, de l'Energie et de la Mer, 2012), we defined wetlands covered with either grassland or forest as active riparian areas, thus excluding croplands from retentive riparian areas. Figure 3a and b show the extension of the thus-defined active riparian wetlands for the whole Seine-Normandy watershed and for the Haut Loir basin. The same procedure was followed for the Red River basin, using the global SRTM 90-m digital elevation model (Jarvis et al., 2008) and land use data from Chanan et al. (2014) (Fig. 3c).

From this information, the surface area (and volume, considering the 0.3-m active layer) of active wetlands can be calculated for each unit watershed in the basin under investigation (Table 1).

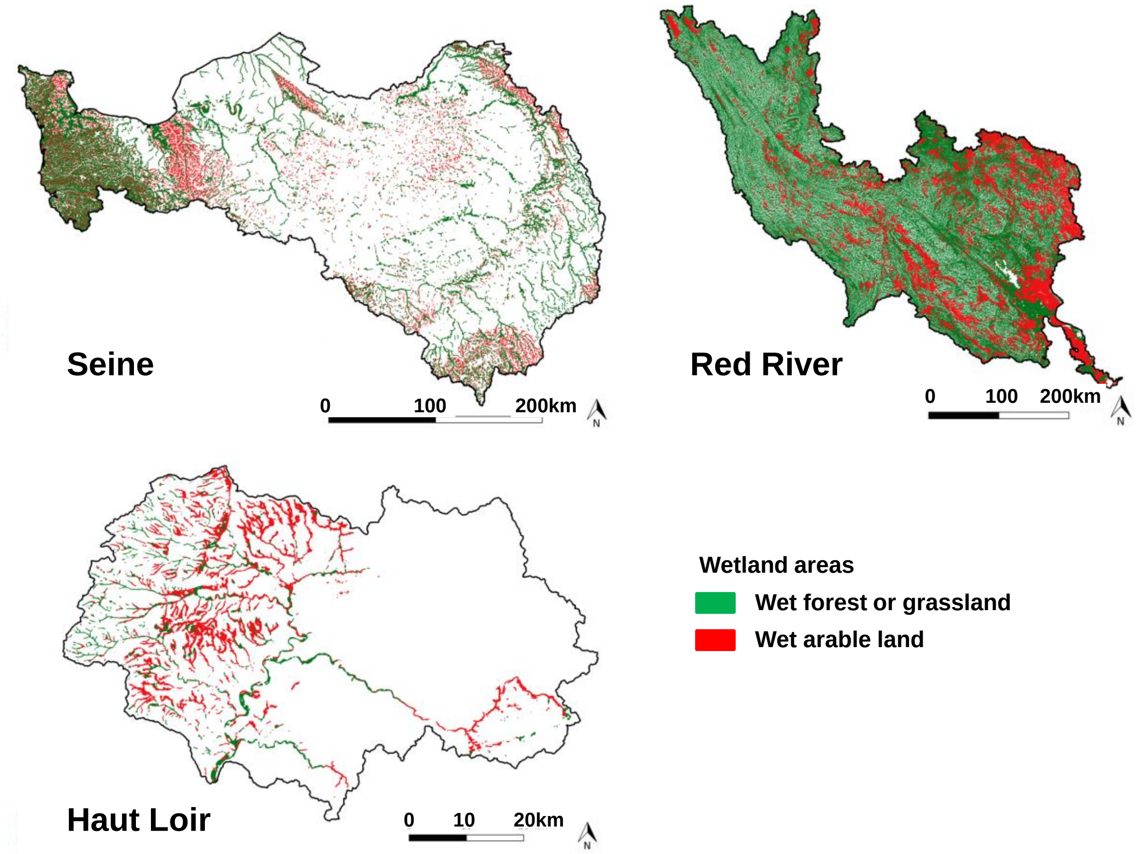

Figure 3. *Riparian wetland zones in the Seine-Normandy, Haut Loir and in Red River watersheds. Riparian wetlands covered with forest or grassland are represented in green: these are considered as active retention zones. In red are wetlands occupied by cropland, considered as non retentive for nitrate flows from the watershed.*

Tile drainage has been widely implemented in cropland areas with low permeability in order to improve soil agronomical properties by removing excess water in early spring. The result is an increase of surface runoff and its direct routing to surface water through ditches, thus by-passing riparian wetlands. Figure 4 shows the extension of tile drainage at the scale of the Haut Loir and Seine-Normandy basins, based on the data of the Agricultural Census of 2010 (http://agreste.agri-culture.gouv.fr/recensement-agricole-2010/). Tile drainage is not present in the Red River basin.

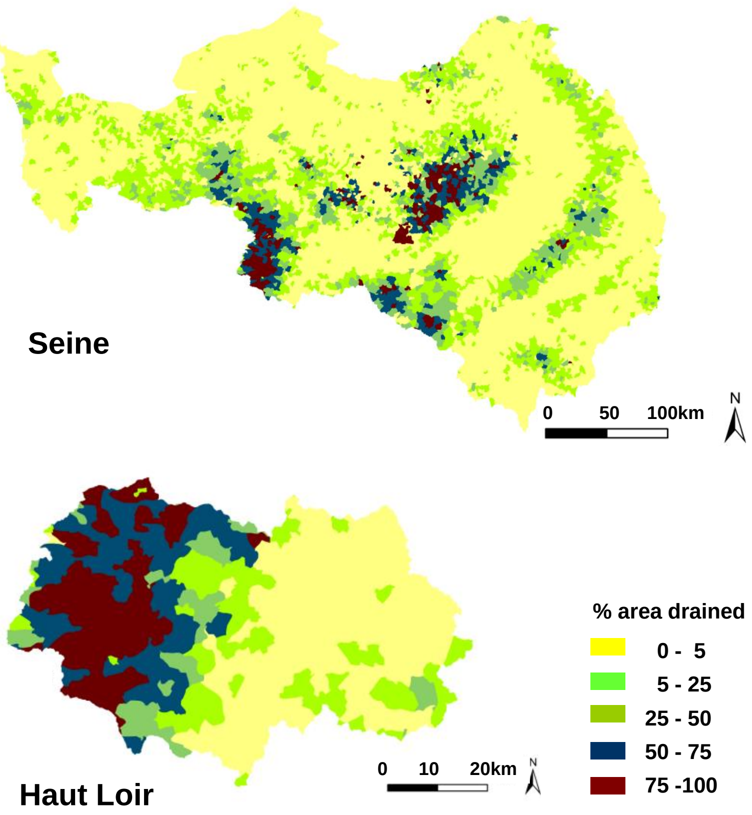

Figure 4. *Extension of tile drainage, expressed as % cropland area equipped in the Seine-Normandy watershed (a) and the Haut Loir sub-basin (b). (data from Agricultural Census, 2010, Agreste)*

3. Potential denitrification rate

As explained above, the quantitative formulation of riparian retention requires assessing a value of the potential denitrification rate of wetland soils, under water saturation conditions, anoxia and a non-limiting concentration of nitrate. A literature survey was carried out for that purpose.

3.1. Measurement of soil denitrification potential

Many measurements of soil denitrification potential, often called denitrifying enzyme activity have been reported in literature. The original protocol proposed by Tidge (1982) consists of incubating the soil sample as a slurry with a de-oxygenated nitrate-rich solution, and measuring denitrification either by following the decrease of nitrate concentration in the solution or by measuring N_2O production under inhibition of the last step of denitrification by acetylene. Many modifications of the protocol have been introduced, sometimes involving addition of labile organic matter substrates(Pell et al., 1996), which usually results in only slightly higher denitrification potential (Clément et al., 2002; Ullah & Faulkner, 2006; Laverman et al., 2010; Wu et al., 2013). Measurements (Table 2) show a very wide range of values, from less than 0.01 to more than 1 µgN/gsoil/h.

Table 2. *Potential denitrification rate measured at 20°C in the top layer of agricultural or riparian soils in slurry, with or without addition of labile organic substrate.*

Soil	**Location**	**%Corg**	**denit pot** µgN/g/h	**Method** Detection method	Org substr	**Reference**
Riparian strip, morainic landscape	DK	30–34 (totC)	1.3–6.1	C2H2 block	with	Ambus (1993)
Riparian soils	USA, lower Mississippi					Ullah & Faulkner (2006)
forested wetlands		3.3	1.18	C2H2 block	without	
depressional wetlands		1.7	0.77	C2H2 block	without	
constructed wetlands		1.2	0.82	C2H2 block	without	
veg ditches		1.2	0.66	C2H2 block	without	
unveg ditches		1.6	0.5	C2H2 block	without	
ag-low		1.4	0.4	C2H2 block	without	
ag-high		0.6	0.16	C2H2 block	without	
Agricultural Lanton soil	USA	4.3	0.09	C2H2 block	with	Murray et al. (1989)
Agricultural Maury soil	USA	1.9	0.01	C2H2 block	with	
Sandy soil (Melby)	SW	1.9	0.29	C2H2 block	with	Pell et al. (1996)
Silty-clay soil (Lanna)	SW	2.2	0.52	C2H2 block	with	
Heavy clay soil (Ekhaga)	SW	4.1	3.0	C2H2 block	with	
Agricultural soils	France					Hénault et al. (2001)
Villamblain	Beauce	1.4	0.21	C2H2 block	without	
Arrou		1.1	0.31	C2H2 block	without	
La Saussay		1.2	0.11	C2H2 block	without	
eutric leptosol	Bourgogne	3.09	1	C2H2 block	without	
gleyic luvisol		0.86	0.15	C2H2 block	without	
rendzic leptosol		1.67	2	C2H2 block	without	
cultivated calcaric fluvisol		3.34	2	C2H2 block	without	
cultivated gleyic cambisol A		1.52	0.4	C2H2 block	without	
cultivated gleyic cambisol B		1.99	0.5	C2H2 block	without	
grassland calcaric fluvisol		5.18	5	C2H2 block	without	
grassland gleyic cambisol A		2.38	1.2	C2H2 block	without	
grassland gleyic cambisol B		3.03	1.2	C2H2 block	without	
Slope transect Morand River	CH		0.61	C2H2 block	with	Cosandey et al. (2003)
			0.085	C2H2 block	with	
Loamy riparian soils	B					Dhondt et al. (2004)
mixed vegetation, III 0–30 cm		4.5	0.170	C2H2 block	without	
mixed vegetation, II 0–30 cm		6.4	0.200	C2H2 block	without	
mixed vegetation, I 0–30 cm		2.5	0.125	C2H2 block	without	
forest, III 0–30 cm		2.2	0.175	C2H2 block	without	
forest, II 0–30 cm		2.9	0.25	C2H2 block	without	
forest, I 0–30 cm		3.4	0.175	C2H2 block	without	
grassland, III 0–30 cm		5.8	0.188	C2H2 block	without	
grassland, II 0–30 cm		5.15	0.196	C2H2 block	without	
grassland, I 0–30 cm		3.2	0.167	C2H2 block	without	
Clayey riparian soils river Han	China					Liu et al. (2016)
agricultural riparian soils		2.3	0.0028	C2H2 block	with	
forested riparian soils		1.7	0.00066	C2H2 block	with	
Restored forest wetlands	NC, USA					Sutton-Grier (2010)
Charlotte		7.4	0.19	C2H2 block	with	
Duke		11	0.54	C2H2 block	with	
Riparian and slope soils	Brittany, F					Oeler et al. (2009)

riparian		2.9	0.18	C2H2 block	with	
hill slope		2.3	0.12	C2H2 block	with	
Loamy clay riparian wetland	Brittany, F					Clement et al. (2002)
uphill		3.0	1.4	C2H2 block	with	
hillslope		5.5	2.5			
riparian		6.1	4.8			
Garonne floodplain	F		0.01	C2H2 block	with	Pinay et al. (2000)
			0.15			
Agricultural Luvisol	Brie, F	1.9	0.11	NO3 cons	without	Benoit et al. (2015)
Agricultural Luvisol	Brie, F			NO3 cons	without	Vilain et al. (2012)
topsoils (10–30 cm)		1.2	0.68			
subsoils (40–110 cm)		0.43	0.61			
Agricultural Luvisol	Brie, F			NO3 cons	without	Vilain et al. (2014)
Rip20		1.42	0.6			
Rip100		0.4	0.5			
Foot20		1.12	0.35			
Foot100		0.75	0.1			
slope20		1.42	0.7			
slope100		0.4	0.2			
organic20 (Jan 2010)		1.19	0.7			
organic1200		0.39	0.5			
conv20 (Jan 2010)		1.2	0.8			
conv100		0.53	1			
forest20		2.48	1.7			
forest100		2.78	2.6			
grassland 20		0.86	1			
grassland 100		0.4	1.5			
organic20		1.19	1.55			
organic100		0.39	0.9			
conv20 (March 2011)		1.21	1.5			
conv100		0.53	0.25			

Within a single group of sites with similar pedogenetic conditions, measurements often show an increase in denitrification potential with increasing soil organic C or fine particle content (Dhondt et al., 2004; Ullah & Faulkner, 2006), but this effect is not perfectly clear for all the measurements available in the literature (Fig. 5), confirming the conclusion of several authors that denitrification in soils cannot be predicted from a limited number of factors such as carbon content, texture, pH (Knowles, 1982; Simek et al, 2000) but depends on a complex set of properties, namely those linked to their landscape position (Florinsky et al., 2004; Ullah & Faulkner, 2006; Oeler et al., 2008).

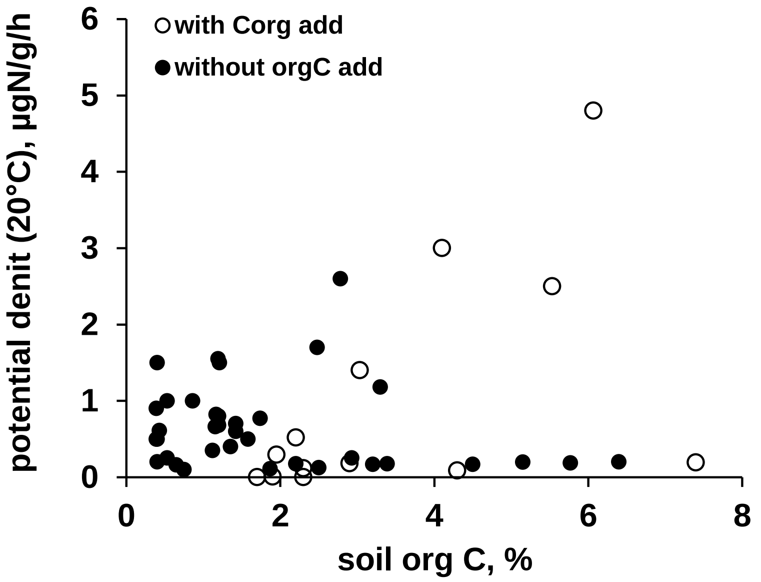

Figure 5. *Potential denitrification rate (slurry method) in the top layer of agricultural or riparian soils, as a function of their organic C content, measured with (open symbols) or without (black symbols) addition of labile organic substrate.*

Another difficulty lies in the fact that the denitrification potential of riparian soils, measured on homogeneous samples in slurry, is not fully expressed under natural conditions, namely because of the preferential water path through soil interstices or macroporosity (Willems et al., 1997; Haag & Kaupenjohann, 2001). Therefore, Ambus (1993) indicates that measurements on intact soil cores show values typically 10–20 times lower than those carried out on slurry, while Vilain et al. (2014) found the same order of magnitude for cores and slurries. Henault & Germon (2000), Clement et al. (2002) and Oeler et al. (2007) also report a 2- to 3-order of magnitude difference between the potential and effective *in situ* value of denitrification.

We conclude from this brief literature survey that *a priori* defining a denitrification potential for riparian soils is very difficult, although a value of about 1 µgN/g/h, at 20°C appears to be a maximum under saturating nitrate concentration, i.e., a value of 400 mgN/m²/h, taking into account an apparent density of 1.4 g/cm^3 and an active soil depth of 0.3 m.

3.2. Effect of nitrate concentration and temperature

In their review paper on groundwater denitrification, Rivett et al. (2008) estimate that denitrification obeys zero-order kinetics as long as the nitrate concentration remains above a threshold of 1 mgN/l. Half-saturation constants (Km) measured on slurries indeed show very low values (<0.1 mgN/l) (Murray et al., 1989; Ambus, 1993), which is confirmed by the observation that the linear shape of nitrate decreases in slurry experiments. Although this is in contradiction with the hypothesis of the NEMIS model (Henault & Germon, 2000; Oehler et al., 2009), which considers a Michaelis-Menten relationship between denitrification and nitrate concentration with a Km of 0.022 mgN/gsoil (roughly equivalent to about 80 mgN/L in the soil solution at field capacity) as measured from the comparison of denitrification rates in intact cores with and without added nitrate, we will consider that the denitrification rate is independent of the nitrate concentration in the water flow as long as it is above 0.5 mgN/L. Denitrification is considered to stop below this threshold.

The denitrification rate is strongly temperature-dependent (Stanford et al, 1975; Rivett et al., 2008). Empirical data gathered in Figure 6 suggest a sigmoid relationship, taking the following form:

$$\text{ftemp} = e^{-[(T-\text{topt})^2 / \text{dti}^2]} \;/\; e^{-[(20-\text{topt})^2 / \text{dti}^2]} \qquad (6)$$

with topt = 45°C (± 5°C) and dti = 24°C (± 4°C)

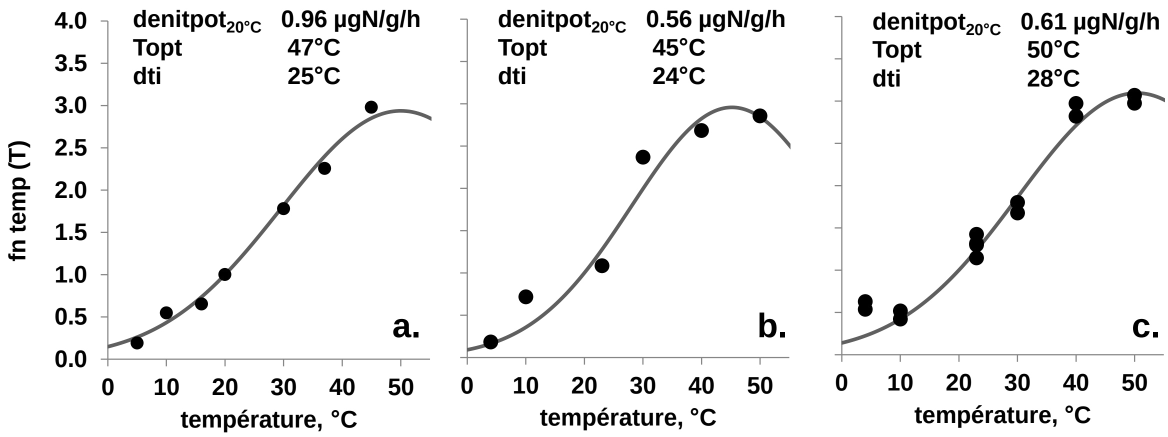

Figure 6. *Temperature dependency of the potential denitrification rate (measured in slurry) in different soil samples. The function fntemp(T) is defined as the ratio between the rate measured at temperature T with respect to the rate at 20°C. (a) Plateau luvisol in Brie (Benoit et al., 2014); (b) alluvial meadow soil in Brie (this study); (c) riparian soil in Brie (this study).*

Implementation and application of the model

The concepts developed above for taking into account riparian retention of diffuse sources of nitrogen from the basin have been implemented as a new version of the Riverstrahler model, called Seneque 3.7. For each elementary watershed (the drainage area of a segment of river between two confluences, or from the spring to the first confluence), at each 10-day period, the flux of nitrate accompanying surface and base flow runoff (calculated based on the average sub-root concentration of each land use class), is compared with the potential denitrification rate of the riparian wetland area of the same elementary watershed given the water temperature at that moment of the seasonal cycle, and considering an adjustable parameter representing the riparian soil potential denitrification (in $mgN/m^2/h$). Only nitrate in excess over this denitrification potential reaches the surface water. If a certain fraction of the elementary watershed is tile-drained, this fraction of the superficial water flow is considered to by-pass the riparian zone. In this calculation, the value of the denitrification potential is the single adjustable parameter, whose value is expected to be far below 400 $mgN/m^2/h$. For the sake of simplicity, the same value of this parameter is considered over the entire watershed.

1. Application to the Haut Loir watershed

The distribution of the nitrate concentration in sub-root water in the Haut Loir basin was calculated, as explained above, from the soil N balance of each crop rotation class in the basin considering an average infiltration water depth of 130 mm/year (Fig. 1). With this input, the model provides a satisfactory simulation of the winter high-water nitrate concentration level, which at that period is close to the average sub-root nitrate concentration. Observed seasonal variations of the river nitrate concentration are very pronounced in the northwest area of the basin; they have a much lower amplitude in the eastern part. The model captures these variations well for a value of the riparian denitrification potential at 20°C set within the range 0.75–1.5 $mgN/m^2/h$. (Fig. 7), for which the RMSE of the simulation is the lowest (see Fig. 8).

The simulation by the model with the riparian denitrification potential set at zero indicates what would be the nitrate concentration in the absence of any riparian denitrification, with only in-stream benthic denitrification processes occurring. In the case of the Haut Loir basin, seasonal variations simulated without riparian retention are quite minor, indicating very low in-stream denitrification processes. The comparison of the model simulations with and without riparian denitrification thus allows calculating the average annual budget of nitrogen transfer and retention in the watershed (Table 3).

For the Haut Loir basin, riparian retention amounts to 55–85 kgN/km²/yr, i.e., 7–11% of the annual nitrate flux leached from the basin. The sensitivity of this estimation of riparian retention with respect to the value of the denitrification potential is illustrated in Figure 8.

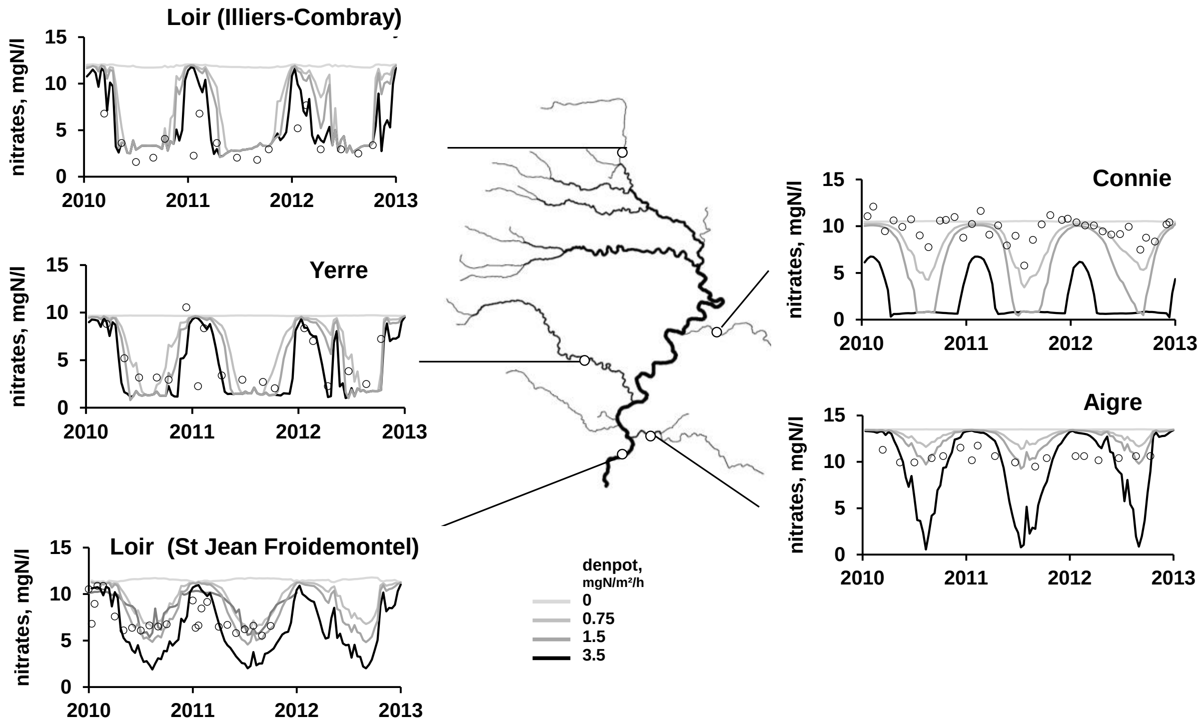

Figure 7. *Simulation by the Seneque 3.7 model of the seasonal variations of the nitrate concentration at different stations of the Haut Loir river network, for different values of the potential denitrification rate of active riparian areas (from 0 to 3.5 mgN/m²/h*)

Table 3. *Budget of nitrogen transfer and retention in the three watersheds over the 2009–2011 period, as estimated from the simulation with Seneque 3.7 of the nitrate concentration with and without riparian denitrification.*

	Haut Loir (at St Jean)	**Seine** (at Poses)	**Red River** (at Hanoi)
Total area, km²	3590	67700	139 000
Average leaching, kgN/km²/y	760	1620	2023
Riparian retention, kgN/km²/y	55-85	150	1072
Urban point sources, kgN/km²/y	40	830	586
In-stream retention, kgN/km²/y	10-50	530	350
Delivery at the outlet, kgN/km²/y	695-725	1770	1187

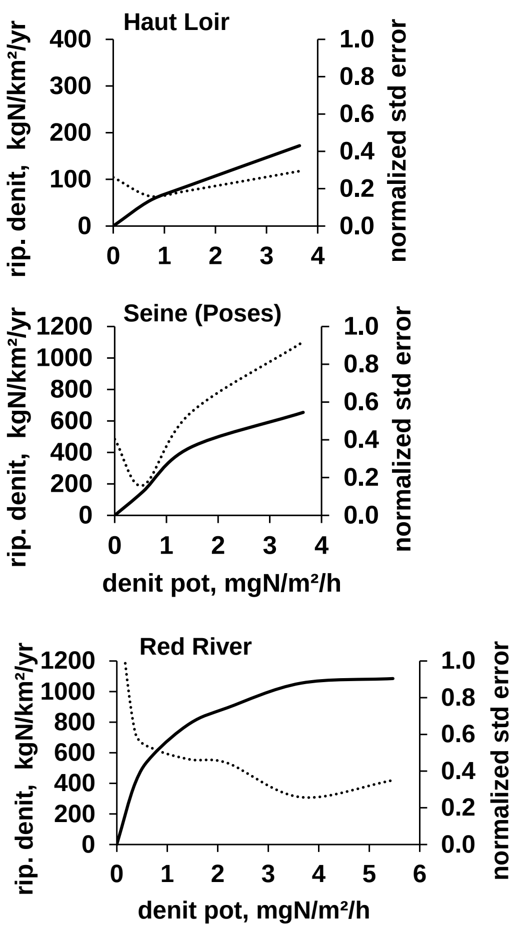

Figure 8. *Sensitivity of the annual riparian retention rate over the whole watershed estimates with respect to the value of denitrification potential for the Haut Loir (a), the Seine (b) and the Red river (c) watersheds. The normalized root mean square error of the simulations with respect to the observed nitrate concentration is also plotted (dotted line): its minimum indicates the most likely value of the denitrification potential.*

2. Application to the whole Seine-Normandy watershed

The application of the model to the whole Seine-Normandy basin is based on a coarser definition of land use classes, derived from the Corine Land Cover 2012 GIS layer (Ministère de l'Environnement, de l'Energie et de la Mer, 2012), distinguishing between forest, urban areas, arable land and grassland. For the two latter land cover types, the N soil surpluses were calculated by Le Noë et al. (2017) from agricultural statistics using the GRAFS methodology, at the scale of homogeneous agricultural areas, and converted into the nitrate concentration in the sub-root water taking into account the average infiltration depth of the corresponding regions (Fig. 2b).

Here again, the model run with zero riparian denitrification provides a good simulation of the winter level of the nitrate concentration everywhere in the watershed, even though this level varies widely, between 4 and 11 mgN/l, in the different tributaries (Fig. 9). The model captures the pronounced seasonal variations of nitrate concentrations well for a potential denitrification value at 20°C of about 0.75 mgN/m²/h (stRMSE= 0.15, Fig. 8b). This value of the parameter (very close to the one selected for the Haut Loir application) allows the model to catch the substantial differences observed between the seasonality of nitrate variations in the different parts of the basin, with much lower differences between winter and summer values in some downstream stations (Oise, Eure) than in upstream tributaries (Yonne, Marne, Seine, Loing).

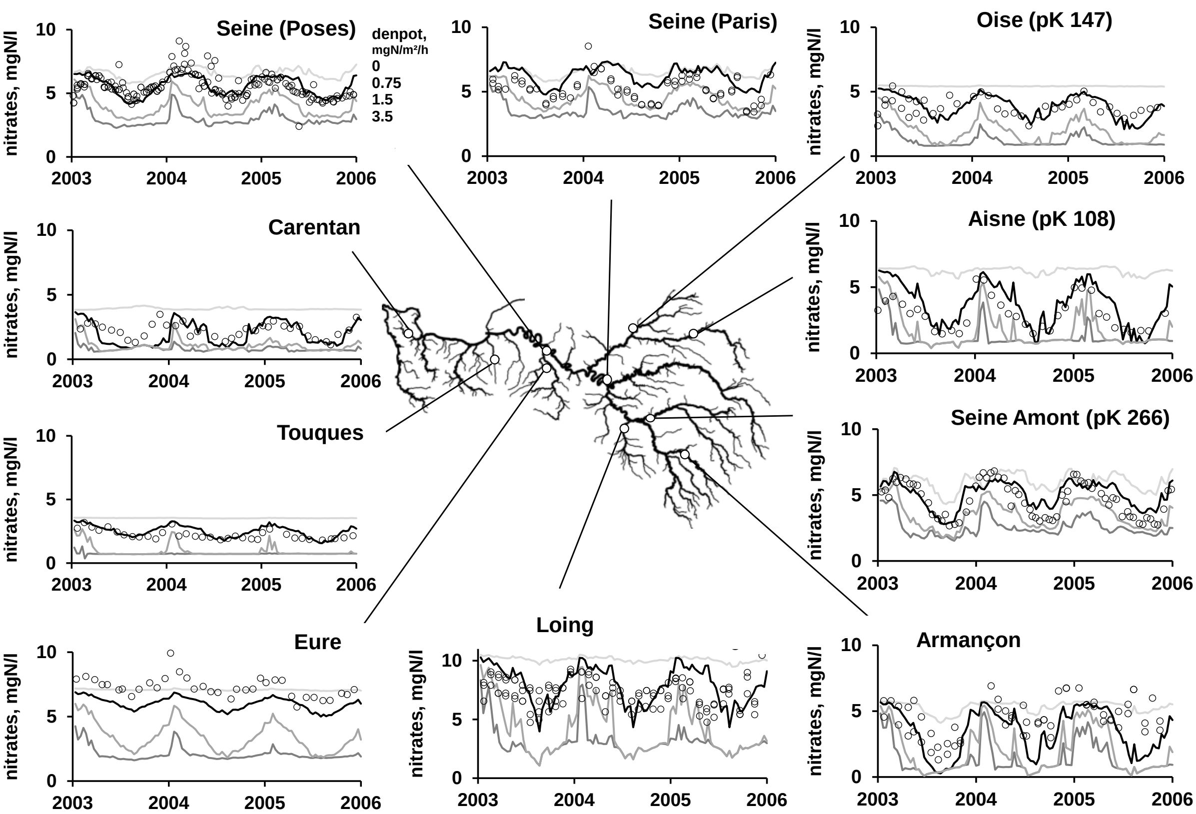

Figure 9. *Seasonal and interannual variations of nitrate concentration at several stations of the Seine River network simulated by the Riverstrahler model, for four values of the potential riparian denitrification rate (0, 0.75, 1.5 and 3.5 mgN/m²/h).*

Based on these simulations, the average N transfer budget has been established for the Seine watershed at the entrance of the estuarine zone (station Poses) (Table 3). The sensitivity of the estimation of the annual riparian denitrification rate with respect to the value taken for the potential denitrification rate of riparian zones is illustrated in Figure 8b.

3. Application to the Red River system

For the Red River basin, an even coarser approach was used to define the spatial distribution sub-root concentration, as described by Le et al. (2005) (Fig. 1c). Using these input data, together with the wetland distribution calculated from the DEM (Fig. 3c), provides a reasonable agreement of the general level of calculated nitrate concentrations with observed values at the outlet of the major branches of the Red River system (Fig. 10), for a denitrification potential value close to 4 mgN/m²/h, significantly higher than the value used for the other two watersheds. The Red River system is characterized by its tropical hydrological regime, with high discharge during the summer period and much higher specific runoff values than in the previous two temperate watersheds. The nitrate concentration remains at rather low levels in all tributaries of the Red River and show only limited seasonal variations compared with temperate rivers.

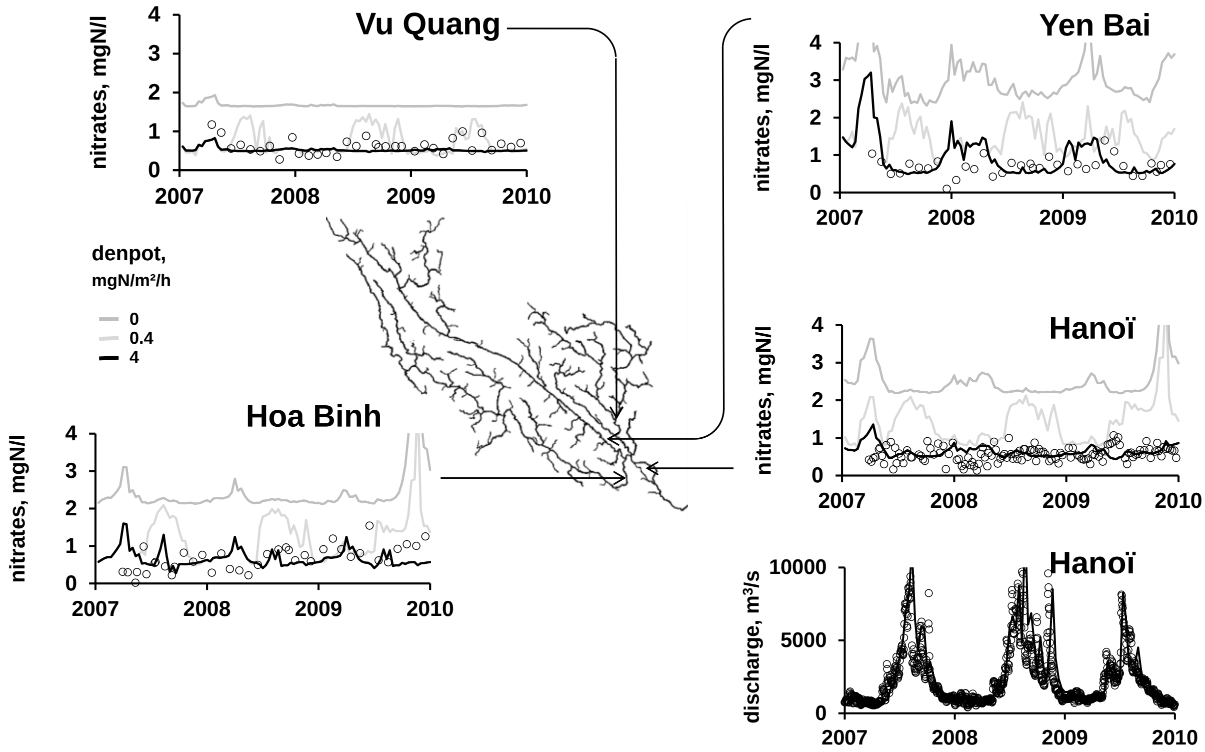

Figure 10. *Seasonal and interannual* variations *of the nitrate concentration at four stations of the Red River network (Vietnam) simulated by the Riverstrahler model, for different values of the potential riparian denitrification rate (0, 0.4 and 4 mgN/m²/h). The other parameterizations of the model (hydrological and climatic conditions, diffuse and point sources of nutrient and organic matter) are those proposed by Le et al. (2010). Water discharge variations at the Hanoi station are also shown.*

Lower values of the potential denitrification in this sub-tropical basin would provide higher river nitrate concentrations than observed during summer high discharge periods. Owing to higher temperatures and a coincidence of high specific discharge with high temperature, which is characteristic of a tropical runoff regime, the calculated effect of wetland denitrification on river water nitrate is quite significant, because it reduces the concentration of infiltrated water by a factor of 3–5 throughout the year, and not only at low discharge periods. A wider extent of riparian areas, particularly in the delta region of the basin (Fig. 3), also plays a role in this important riparian denitrification. As a whole, riparian denitrification accounts for about half the total nitrogen leaching from watershed soils (Table 3).

Discussion and Conclusion

Groffman et al (2009) stressed the challenge to measure and model denitrification at regional scale arising from the fact that hotspots (small areas) and hot moments (brief periods) account for a high proportion of the total annual denitrification. This is indeed the challenge for modelling riparian denitrification at the watershed scale. The approach we present in this paper is based on the identification of potential wetlands (essentially defined from topographic attributes) as the major hotspots for denitrification in the landscape. The hot moments are those when high nitrate fluxes (most often associated with high water fluxes) from the watershed coincide with high denitrification capacity of the riparian soils (highly dependent on temperature). Our model thus offers an elegant way to calculate the cumulated effect of these seasonally and spatially highly variable processes at the watershed scale.

It simulates nitrate seasonal variations in the river network over a wide range of geographical scales, and with different strategies used to represent the diffuse agricultural sources of nitrate. In the three examples chosen in this paper, the model results offer a reasonable fit not only with the observed concentration levels, but also with their pattern of seasonal variations, which can vary widely between tributaries of a single watershed, namely owing to the distribution of riparian wetlands, the water runoff regime or the presence of tile drains in some areas.

Our model is based on the same principles as those expressed by Ranalli et al (2010) who highlighted the crucial role of the interaction of groundwater with soil labile organic matter, so that denitrification is very active in the upper riparian soil layers, but remains negligible in deep groundwater. These authors indicated that nitrate attenuation in groundwater traversing the riparian zone varies in its effectiveness according to the hydrogeologic properties of the riparian zone and its position with respect to groundwater flow systems. Such approaches do not consider the case of denitrification by riparian areas during periods of overbank flow. Vidon & Hill (2004, 2006) proposed a conceptual model consisting of a typology of riparian zone based on topographic, soil, surficial geology, and vegetation maps to determine landscape attributes linked to nitrate removal efficiency. Our quantitative approach is much simpler operationally since it requires only the spatial distribution of active wetlands, obtained from topography and land cover GIS information, and the calibration of one single parameter related to potential denitrification rate of wetland soils.

In the two temperate basins, the Seine and Loir watersheds, a value within the range 0.75–1.5 $mgN/m^2/h$ is the best adjustment of the potential denitrification parameter to fit the observed data. In the subtropical Red River basin, higher values, within the range 4–5 $mgN/m^2/h$ are required, probably indicating much more active riparian soils under these conditions. Both values are compatible with those reported in the literature for potential denitrification measured on soil samples in the laboratory. Although the goodness of fit of these simulations could certainly be improved, in particular with a better definition of the nitrate leaching from cropland, these results show the high genericity of the modeling approach proposed in this paper, which is able to simulate the seasonal variations of nitrate submitted to riparian denitrification at different scales and under quite different climatic and hydrological conditions.

Furthermore, the modeling approach quantifies the role of riparian retention in the N cascade from watershed soils to the river outlet. According to the N budgets established from the model, riparian retention eliminates between 10 and 15% of the diffuse sources of nitrogen into the hydrosystem through soil nitrate leaching in the two temperate basins studied; in the tropical Red River, riparian retention amounts to 50% of diffuse N sources (Table 3). By comparison, Weller et al (2011) using statistical models linking cropland area, presence of riparian buffer and river nitrate concentration, estimated that riparian buffers currently remove 5 to 50 % of the nitrate inputs from cropland in the Chesapeake Bay watersheds (USA). In-stream retention represents 17, 23 and 22% of total N loading in the Haut Loir, Seine and Red River watersheds, respectively.

In our three example watersheds, the leaching rate of cropland areas was estimated as an average to 11, 32 and 46 kgN/ha/yr, in the Haut-Loir, the Seine and the Red River watersheds respectively (combining data from Table 1 and 3). The denitrification rate estimated per ha of active riparian wetland in the 3 watersheds is respectively 23, 21 and 50 kgN/ha/yr. Although we are far from a five time more efficient rate per ha, this is enough however to attenuate 9-53% of the total nitrate load in wetlands occupying 3 to 20% of the total watershed area. In view of the very contrasted characteristics of the 3 basins studied here, these values can be reasonably considered as indicative of the range of riparian nitrate attenuation at regional scale.

Our study is focused on the processes occurring during the transit of groundwater from agricultural plateaus to the river, across riparian zones. Yet, the story is not finished once this step has been taken, and nitrates have reached surface water. Denitrification in the benthic zone of the drainage network itself, including its hydrological annexes such as ponds, lakes, surface water connected wetlands and surface transient storage zones, can play a further significant role in nitrogen removal (Wollheim et al., 2014). This issue was previously addressed with the Riverstrahler model by Passy et al. (2012) who simulated a 25% reduction of the annual nitrogen flows for a scenarios of pond restoration in rural landscapes at a density of 5% of the agricultural area. More recently, Czuba et al (2018) and Hansen et al (2018) have shown how the collective biogeochemical functioning of the network of reaches and connected hydrological annexes, with shifts between nitrate, organic carbon and residence time limitation of nitrification, could lead to extremely efficient nitrate removal at the watershed scale. All these results converge to conclude that wetlands (open water or riparian) may be more efficient per unit area than the most effective land-based nitrogen mitigation strategies including land retirement from agriculture. The possible side effects of enhanced N_2O emissions could however be kept in mind when deciding between curative or preventive management strategies (Garnier et al., 2014).

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