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Impact of Fertilizer Application and Agricultural Crops on the Quality of Groundwater in the Alluvial Aquifer, Northern France

**Jamal El Khattabi · Barbara Louche ·
Hanan Darwishe · Fadi Chaaban · Erick Carlier**

Abstract In France, the quality of water resources with respect to nitrates deteriorated between the beginning of 1970s and 2000s. A stabilization of the situation and of the improvements has been observed punctually since the 2000s. Despite the application of the Nitrates Directive in France (91/676/CEE), the overall situation remains degraded, with numerous increases in nitrate concentrations in the underground waters. In the North of France, an alluvial groundwater's nitrate concentration exceeds the drinking water limit fixed at 50 mg/l, in the sectors of Catillon-sur-Sambre and Rejet-de-Beaulieu. In order to quantify and model the impact of agricultural nitrogen on groundwater, an approach based on an integrated model has been established using three specific codes for each lithological horizon: Agriflux (for the root zone), VS2DT (for the unsaturated zone), and ModFlow-MT3D (for the saturated zone). The results illustrate the sensitivity of quality to agricultural crops used. Based on scenarios over 20 years, the predictions show a link between nitrate concentrations in the groundwater and agricultural crops as well as fertilization. Improving quality with a concentration of nitrate less than 50 mg/l requires a reasoned management accompanied by rotations of crops and transformations into grasslands and for sensitive areas the use of the culture producing the least nitrogen flow such as beets. The integrated model constitutes an efficient tool for predicting the evolution of the groundwater quality, especially in sensitive areas like the valleys with a rapid nitrate transfer to the aquifer. The model makes it possible to correctly evaluate the concentrations of nitrates reaching the groundwater with a monitoring of the concentration evolution in each lithological horizon, thus constituting a good tool for the management of agricultural pollution.

Keywords Nitrate · Fertilization · Agricultural crops · Water quality · Alluvial aquifer · Modeling

J. El Khattabi (✉) · B. Louche
Civil Engineering and Geo-Environment Laboratory (LGCgE),
Polytech'Lille, Lille University—Science and Technology, avenue
Paul Langevin, 59650 Villeneuve d'Ascq, France
e-mail: jamal.elkhattabi@polytech-lille.fr

H. Darwishe
Faculty of Civil Engineering, Al-Baath University, Homs, Syria

F. Chaaban
Faculty of Civil Engineering, Tishreen University, Lattakia, Syria

E. Carlier
Laboratoire de mécanique multi-échelles et multi-physiques
(LamCube), Polytech'Lille, Lille University—Science and
Technology, avenue Paul Langevin, 59650 Villeneuve d'Ascq,
France

1 Introduction

Groundwater is prone to surface pollution since much of its renewal is by effective precipitations that fall to the surface and infiltrate through the ground up to groundwater, taking with her some highly soluble products such as nitrates. Spreading fertilizer and pesticides in excessive quantities are common examples of

contamination diffuse which can affect the quality of groundwater (Bonton et al. 2011).

Nitrogen is an element used to fertilize agricultural land; it is found everywhere in the planetary ecosystem, even in its natural state. It is one of the nutrients essential for plant growth. Excess nitrogen in the soil will leach and transport as nitrates up to groundwater, since nitrates (NO_3^-) are the most soluble form of nitrogen. Processes for the transformation of nitrogen and of nitrate (NO_3^-) migration differ from one place to another, depending on some parameters such as the nature of the aquifer, topography, and depth of the groundwater (Bernard et al. 2008). The migration of soluble elements in soil water as nitrates can be studied according to these parameters.

Another origin, this time anthropogenic, is related to the urban areas. So, Ford and Tellam (1994) and Lerner et al. (1999) showed that the nitrate concentrations in the groundwater of urban areas are higher than those in the agriculture area. In Denmark, Schroder et al. (1985) infiltration into the aquatic environment was assessed at 15% of urban origin and 85% of agricultural opium. In Europe, the groundwater potability threshold has been set at 50 mg/l by European Framework Directive related to water policy (2000/60/EC).

Several approaches allow evaluating the nitrate transfer from the surface, marked by agricultural activities, to the groundwater using different calculation codes. This is the case of approaches using unitary biophysical models (Laura and Siegel 2006; Almasri and Kaluarachchi 2007; Cho et al. 2010; Bonton et al. 2012; Bernard et al. 2016; Czekaj et al. 2016; Reza Alizadeh et al. 2017), using integrated models (Serhal et al. 2009; Zhu et al. 2017), and using probabilistic/statistical approaches (Carlier and El Khattabi 2005; Carlier et al. 2006; Darwishe et al. 2017).

The evolution of nitrate concentrations in the groundwater of borough of Cambrai's alluvial aquifer, Artois-Picardy basin, observes concentrations exceeding 50 mg/L. This fact makes it difficult to manage drinking water. In the two communes of Catillon-sur-Sambre and Rejet-de-Beaulieu, the quality of the alluvial groundwater depends on agricultural activities (crop type) and sanitation defects in urban areas.

In order to understand both the processes generating this pollution and propose a reasoned management to deal with this pollution, a study on the evolution of the nitrate concentrations of the alluvial aquifer was carried out in Catillon-sur-Sambre and Rejet-de-Beaulieu and will be presented in this paper. An integrated modeling is applied based on a coupling of four complementary numerical models: AgriFlux, VS2DT, Modflow, and MT3D. In order to follow the evolution of the nitrate concentrations in the "soil, subsoil, groundwater" system, simulations were carried out over a 20-year perspective.
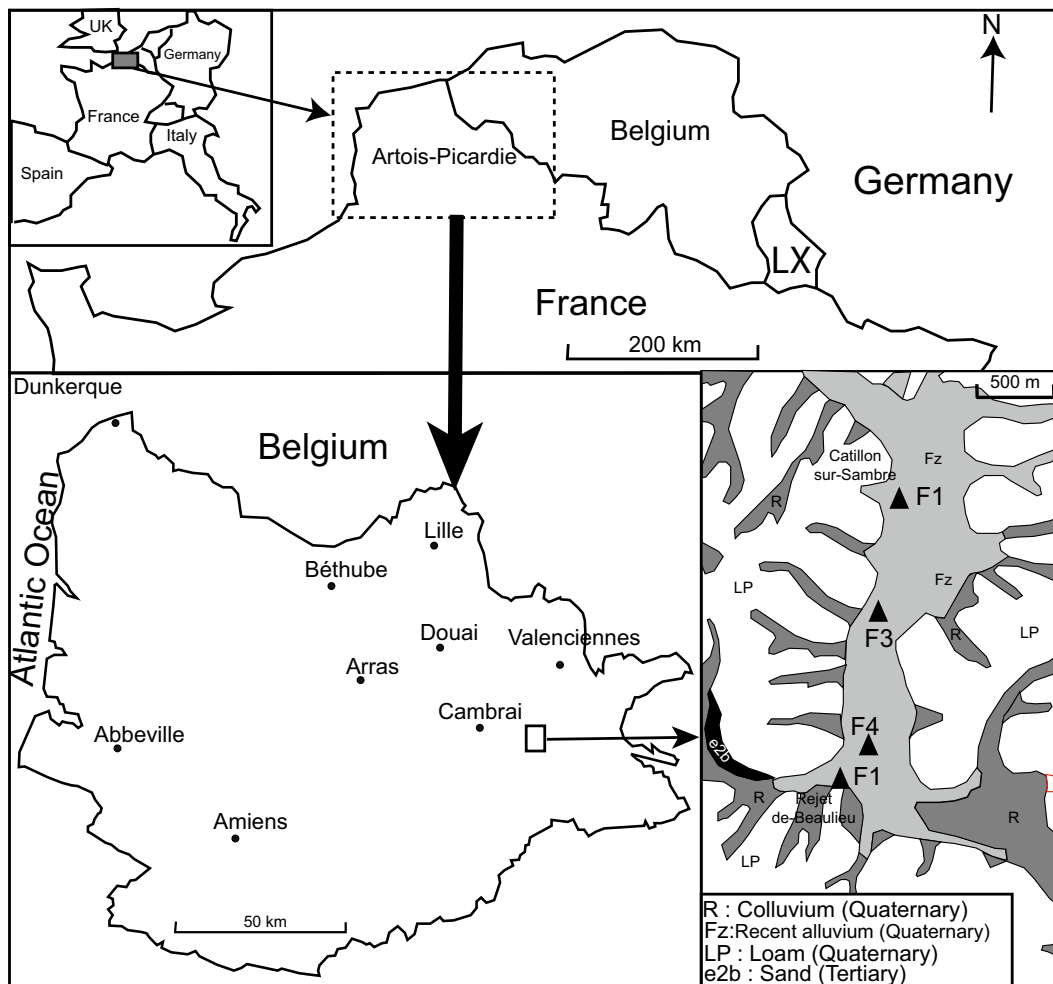
2 Geographical Location and Geological Context

The "Cambrai district" is composed of 115 towns, covering a surface area of 900 km^2 (Fig. 1). A vast plateau in the West and an undulating sector in the East of "Le-Cateau" characterize the relief of the district. The general declivity is directed southeast (+ 186 m) towards north (+ 33 m). The area is characterized by a moderate oceanic climate. The average annual temperature is 9.7 °C with monthly extreme averages of 2.8 °C in January and 17 °C in July. Precipitation varies from northwest to southeast (from 650 to 750 mm), due to wind direction and relief. The subsoil of "Artois-Picardy" basin is essentially composed of Seno-Turonian chalk beneath a layer of silt (or loam), with some areas covered by tertiary formations such as sands and clays (Table 1). The tertiary deposit sectors (Eocene) are important in Flanders until Avesnois.

The study zones, Catillon-sur-Sambre and Rejet-de-Beaulieu, are two municipalities located in the borough of Cambrai. The area of Catillon-sur-Sambre is 13.4 km^2. It lies geographically at an altitude of 149 m. Rejet-de-Beaulieu is a 6.3 km^2 area and it is characterized by 144 m of altitude .

Geomorphology is strongly related to the geological context. Indeed, as Fig. 1 shows, in the valley of Sambre, the seno-Turonian chalk has been eroded and sandy-gravel clayey alluvium rest on the marls of the middle Turonian. Only chalk shards of the upper Turonian were preserved upstream of the valley and on the plateau.

In this sector, we have for the hillsides and plateau the following lands:

- Quaternary silts (or loams) covering the land older than secondary composed of Cretaceous formations belonging to the Turonian
- Upper Turonian chalk on the plateau, North of Catillon-la Groise road, consisting of a chalk with large cornus flint

Fig. 1 Geographical location and geological context

Marl from the Middle Turonian to the south of the road mentioned, and on the flanks of the valley, formed of clayey marls, plastic, waterproof, bluish, or gray, with three intercalary beds of white, heavy, and hard marly chalk.

Table 1 Example of geological succession (boreholes S1, S8, and S10)

Depth (m)	Lithology
0–0.3	Vegetal silt soil
0.3–7.40/11	Sand clayey silt
7.40/11–7.40/13	Chalky silt
7.40/13–8.50/13.50	White-grayish chalk
From 8.50/13.50	White-grayish sandy chalk

In the valley, there are alluvial deposits composed at the head of clay-sandy yellow silts (or loams) and fine sand whose thickness varies from 2.5 to 4 m and can reach locally up to 7 to 8 m covering anterior alluviums more sandy, gravelly, and stony thickness of 3 to 4 m and up to 8 to 10 m thick. They rest directly on the marls of the middle Turonian.

The geological formations previously described are characterized by the existence of an impermeable substratum (Middle Turonian). They contain an almost continuous groundwater with different flows rates: low in recent silt (loam) and alluvium and medium to high (25–80 m^3/h) in ancient alluvia when it is coarse. These last are concentrated essentially in the axial part of the Sambre's valley.

The underground watershed of these formations corresponds substantially to the surface watershed; it

essentially develops on the right bank of the Sambre where all works except the F1 and F2 of Rejet-de-Beaulieu are located.

Climatic data of the area (pluviometry, temperature, and evapotranspiration), characterized by an oceanic climate, were gathered from several weather stations located around the zone of study. Within this study framework, we took into consideration pluviometry and temperature with a decadal time step (from 1 January 1965 to 31 December 2003). It indicates an average annual precipitation of 843 mm and an evapotranspiration of 634 mm (Table 2).

The main characteristics of wells and boreholes are listed below:

– F1 Catillon-sur-Sambre: It is constituted by a well of two meters of intern diameter, deep in 12.5 m. The sandy clay overlay on the gravel and sand is 5.2 m. A rate flow of the order of 70 m^3/h is conceivable. It is characterized by a transmissivity of the order of 6.10^{-3} m^2/s and a specific storage (Ss) of 2%.

– F3 Catillon-sur-Sambre: The covering of sandy clay yellow to gray on the gravel and sand is 8 m. The critical operating flow in this drilling is 30 m^3/h. It is characterized by a transmissivity of the order of 4.8×10^{-3} m^2/s and a specific storage (Ss) of 5%.

– F1 Rejet-de-Beaulieu: It captures the layer contained in the cracks of the upper Turonian chalk, covered by 6.3 m of gray flint clay. Flow tests have

shown low transmissivity (10^{-4} m^2/s). The exploitation flows are 20 m^3/h.

– F4 Rejet-de-Beaulieu: It captures the sandy-gravel alluvium of the Sambre. The loam, clay-sandy, and clay cover are 8 m. Long-term pumping has made it possible to determine the characteristics of the aquifer, which are as follows: transmissivity 4.7 10^{-3} m^2/s and specific storage (Ss) 2.5%.

3 Material and Methods

To better simulate nitrogen transfers in different geological horizons, this work was based on an integrated model coupling three codes (Fig. 2): Agriflux (for the root zone), VS2DT (for the unsaturated zone), and ModFlow-MT3D (for the saturated zone).

We collected the agricultural practice histories (rotation and fertilization) by carrying out inquiries. In addition to the agricultural nitrogen calculated by the model AgriFlux (Banton et al. 1993), the nitrate flow issued from urban activities (domestic and industrial) was also taken into consideration. Flows of water and nitrates are introduced in the VS2DT (Healy 1990) to simulate their transfer in the unsaturated zone.

Table 2 Climatic data

Month	Precipitation (mm)	Evapotranspiration (mm)
January	77.61	19.65
February	58.8	23.36
March	52.36	40.14
April	54.32	61.06
May	56.54	84.51
June	62.2	94.42
July	54.17	102.87
August	61.77	93.65
September	83.50	53.77
October	88.73	23.7
November	96.90	19.96
December	99.22	16.52
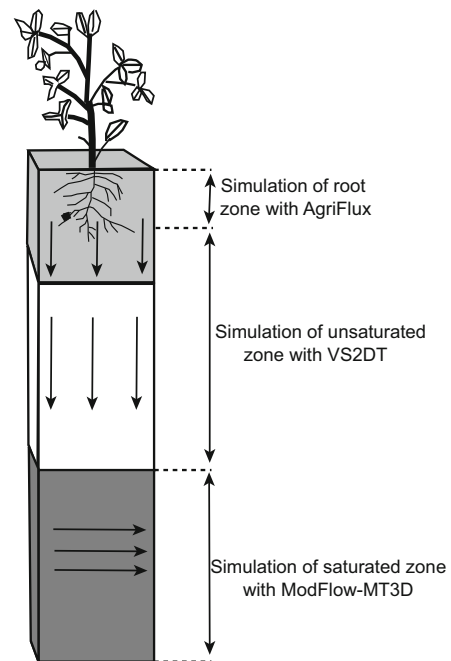
Fig. 2 Integrated model

Finally, the water flows and the nitrate concentrations obtained at the end (bottom) of the unsaturated layer are used as input in ModFlow (McDonald and Harbaugh 1988) and MT3D (Zheng 1990; Zheng and Wang 1999) for the analyses in the saturated zone. A comparison between the calculated and the measured nitrate profile allows us to calibrate the model parameters.

3.1 Models Description

3.1.1 AgriFlux

AgriFlux was used to model the transformation of nitrogen as well as the flow of water and the transfer of nitrates in the root zone (20 cm of deep). AgriFlux is an environmental assessment model developed for the management of diffuse pollution from agricultural sources. Based on a finite difference approach by the reservoirs for the quantitative evaluation of the flows of nitrates reaching the water table, AgriFlux is also a stochastic mechanistic model combining the conceptual representation of mechanisms with the spatial variability of processes and parameters. The type of crop, the quantity of fertilizer, and the climate data were introduced to the model to carry out the various simulations.

In AgriFlux, the variation of the unsaturated hydraulic conductivity according to the water content is calculated using the Irmay cubic relation (Bear 1988):

$$K(\theta) = K_{sat} \left(\frac{\theta - \theta_{cap}}{n - \theta_{cap}} \right) \qquad (1)$$

$K(\theta)$, unsaturated hydraulic conductivity (m/d); K_{sat}, saturated hydraulic conductivity (m/d); θ, layer water content; θ_{cap}, field capacity; n, porosity.

In the unsaturated zone, the denitrification can be accompanied by a production of nitrous oxide during the oxidation of ammonium. In the particular case of nitric nitrogen losses in acid or biological soil, which is more important, this phenomenon can have a chemical origin due to the action of denitrifying bacteria. It is highly influenced by the surrounding soil conditions such as temperature, humidity, organic matter content of soil, oxygen rate, soil morphology, pH, or activity of microorganisms and plants. In AgriFlux, modeling this phenomenon is realized through NitriFlux model, which simulates nitrogen cycle and transport (runoff, mineralization, immobilization, nitrification, denitrification, adsorption of nitrogen by the culture, drainage, and

leaching). This approach is kinetics of the Michaelis–Menten type calculated on daily basis (Johnsson et al. 1987):

$$N_{NO_3 \rightarrow N_2}(z)$$

$$= K_d(z) \, e_{md}(z) \, e_t(z) \left(\frac{[N_{NO_3}(z)]}{[N_{NO_3}(z)] + C_s} \right) \qquad (2)$$

depending on the potential denitrification rate $K_d(z)$, the soil water/aeration status $e_{md}(z)$, and the same temperature factor $e_t(z)$ used for the other biologically controlled processes. The effect of nitrate concentration is controlled by the half-saturation constant, C_s.

3.1.2 VS2DT

This code is used in the modeling of water flow and nitrate transfer in the subsoil, from the underlying layer of the root zone to the roof of the water table. The boreholes realized in the study zone illustrate the presence of the soil formations covering the chalk layer (Table 3).

Results of our simulations are in conformity with the observations in water table. This model combines the law of conservation of the masses with the nonlinear equation resulting from Darcy's law. Works realized by Lappala (1981) on the numerical modeling of flow in unsaturated zone was used in the development of this program:

$$\nu \left[\rho (C_m + s \, S_s) \right] \frac{\partial H}{\partial t} - \rho \sum_{K=1}^{m} A_k K K_r(h) \frac{\partial H}{\partial n_k} - \rho q \upsilon$$

$$= 0 \qquad (3)$$

where υ: volume [L^{-3}], ρ: density [ML^{-3}], $C_m = \frac{\partial \theta}{\partial t}$: water-specific content or variation of water content according to the hydraulic head [L^{-1}], s: saturation [L], Ss: specific storage [L^{-1}], H: total hydraulic head of fluid [L], h: hydraulic head [L], t: time [T], K: conductivity hydraulic at saturation [LT^{-1}], K_r: relative hydraulic conductivity [L], A_K: surface to which n_K is orthogonal, and q: volume of fluid added or taken per unit of volume [L^3].

The resulting mathematical model is developed with the total hydraulic load as a dependent variable. The thickness of the unsaturated zone, the nitrate flows leaving the root zone, are used as data for modeling of nitrate concentrations.

Table 3 Subsoil characters

Geological formation	Porosity	Saturated hydraulic conductivity m/day	Apparent density (kg/m3)	α (m)	β'
Sedimentary overlap (loam)	0.36	1×10^{-7}	1760	1.7	1.25
Aquifer (chalk)	0.42	5×10^{-4}	1600	0.25	1.3

α and β' are parameters of retention curve of Van Genuchten (1980); molecular diffusion of nitrates, 15×10^{-10} m^2/day; longitudinal dispersion in chalk, 5 m

The particle tracking in a porous medium depends on the processes which interact here. Particles can be subjected to deduction (adsorption) or saltings out in the porous medium all along their path (Carlier and El Khattabi 2005; Carlier et al. 2006). The derivative equation of the elementary phenomena during the particle tracking (convection–dispersion) is based on Fick's law and the law of the mass conservation.

The molecular diffusion of the nitrates being 15. The longitudinal dispersivity (10^{-10} m^2 day^{-1}) value was fixed at 5 m.

$$\frac{\partial(\theta c)}{\partial t} = \nabla \theta \overline{\overline{D}}_h \nabla \theta \overline{v} c + q_s \text{with } \nabla = \frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z} \quad (4)$$

where θ = water content, c = dissolved matter concentration, [mL^{-3}], $\overline{\overline{D}}_h$ = hydrodynamic dispersion tensor [L^2 T^{-1}], $\overline{v}$ = vector the speed of liquid [LT^{-1}], and q$_S$ = contribution/deduction [ML$_{-3}$ T^{-1}].

3.1.3 ModFlow and MT3D

The three-dimensional Visual ModFlow model simulates the behavior of underground flows by solving the diffusivity equation using the finite difference method. The MT3D extension of the ModFlow model allows the modeling of concentrations of chemical elements in groundwater. The transfer in the saturated porous layer was carried out using the hydrodynamic model ModFlow. The 3D equation of the groundwater flow used is

$$\frac{\partial}{\partial x}\left[K_X \frac{\partial H}{\partial x}\right] + \frac{\partial}{\partial y}\left[K_Y \frac{\partial H}{\partial y}\right] + \frac{\partial}{\partial z}\left[K_Z \frac{\partial H}{\partial z}\right] - Q$$
$$= Ss \frac{\partial H}{\partial t} \quad (5)$$

where K$_x$, K$_y$, K$_z$: components of saturated hydraulic, conductivity (m s^{-1}); H: hydraulic head (m); Q: voluminal flow per unit of volume, representing the

well/spring term (s^{-1}); S$_s$: specific storage of porous material (m^{-1}); and t: time (s).

On the other hand, the simulation of the nitrate transport in groundwater was carried out by the module MT3D. This model is based on the convection–dispersion equation:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C}{\partial x_j}\right) + \frac{\partial}{\partial x_i}(\mu_i * C)$$

$$+ \frac{q_s}{\omega}C_s - \frac{\rho_b}{\omega}\frac{\partial \overline{C}}{\partial C}\frac{\partial C}{\partial t} - \lambda\left(C + \frac{\rho_b}{\omega}\overline{C}\right) [\text{ML}^{-3} \text{ T}^{-1}]$$
$$(6)$$

where C: solute concentration [ML^{-3}], x$_i$: distance according to the coordinate axis [L], D$_{ij}$: hydrodynamic dispersion coefficient [L^2 T^{-1}], u$_i$: pore velocity according to axis i [LT^{-1}], q$_s$: well/spring term [T^{-1}], Cs: solute concentration in springs or losses [ML^{-3}], ω: kinematic porosity, ρ_b: density [ML^{-3}]: concentration of the pollutants adsorbed by material [ML^{-3}], and λ: constant kinetics of first-order reaction [T^{-1}].

The first simulations are in 2D. Only at the MT3D level, once the flows have reached the underground level, a simulation of the diffusion in the aqueous medium is carried out. This latter will allow us to visualize the spatial distribution of the nitrate concentration.

3.2 Scenarios for Predictions

The results of the application of the transfer of nitrates from the surface to the water table will be followed by predictive simulations. Two scenarios for predicting nitrate concentrations will be considered from the year 2015 to the year 2035:

– The first scenario consists in estimating the soil concentrations towards the groundwater, considering that the whole study area is cultivated during the 20 years of simulation.

– In the second scenario, no crop was considered; just the inputs of nitrogen required to the grasslands were introduced as data.

4 Results and Discussion

The nitric nitrogen (very soluble in water) is considered as the only nitrogen compound that can migrate with water. Ammoniacal nitrogen leached is smaller, because of its ability to be fixed by the soil particles due to the cation exchange capacity or CEC (Barroin et al. 1996). The dynamics of biochemical processes in the soil is controlled by carbon (Ritchie 1991). This one decreases with the depth (Lafrance and Banton 1995); we consider that the nitrates do not undergo any transformation after a given depth.

4.1 Root Zone (AgriFlux)

From a pedology point of view, Table 4 shows the type of soil that we find from the surface at a shallow depth of less than 20 cm. This data is recorded at drilling level. It is very important in the simulation of concentrations in the root zone.

From an agricultural point of view, the data relate to the General Census of Agriculture (GCA); we relied on the census of 2000. According to this GCA, wheat is the main crop in the study area, and it occupies 42% of the area, followed by forage corn and Barley-Bere (Fig. 3a).

Land use has been determined by the cartographic analysis from the Geographic Information System and Environmental Analysis (SIGALE). This analysis is used to locate agricultural parcels and to evaluate the evolution of land use for the years 1990–1998 and 2000–2005. Figure 3b distinguishes urbanized areas from agricultural areas in the two towns Catillon-sur-Sambre and Rejet-de-Beaulieu.

The identification of urbanized areas makes it possible to increase nitrate flows in the model to get closer to the reality. These flows correspond to wastewater discharges. So, based on the work we have done in this area (Serhal et al. 2009), a quantity of 15 kg/ha/year of nitrogen (average rated for the sector) was added to the boreholes located near urban areas. It was applied to borehole F1 Catillon-sur-Sambre and F1 Rejet-de-Beaulieu.

The dominant farming which was noted is the wheat (42% of land use). Other crops are corn (23.9%), barley-bere (11%), sugar beets (7%), and other cereals (16.1%). The quantity of fertilizer applied to each crop is listed in Table 5.

Nitrate concentrations in the root zone were calculated for each parcel. To make the introduction of the data more accessible in the steps that follow the modeling (VS2DT, ModFlow), the nitrate's concentration average was calculated from the root zone for each group of parcels that surrounds catchments. Eight areas were determined (Rejet-de-Beaulieu (F1 and F4), Catillon-sur-Sambre (F1 and F3), Bazuel, Mazinghien, La Groise, and Ors) (Table 4). In this study, we present the results of the simulations carried out on the agricultural fields of Catillon-sur-Sambre surrounding the boreholes F1 (zone 1) and F3 (zone 2) as well as the agricultural lands of Rejet-de-Beaulieu surrounding the boreholes F4 (zone 3) and F1 (zone 4). The simulations were carried out for the period from 1980 to 2010.

Table 4 Corresponds to the superficial fringe extract on the various boreholes

Borehole	Texture	Porosity m3/m3	Field capacity (0.33 bar)	Wilting point (15 bars)	Hydraulic conductivity m/day
F3 (Catillon-sur-Sambre)	Loam, sandy clay	0.398	0.255	0.148	0.1032
F1 (Catillon-sur-Sambre)	Clay becoming sandy at base	0.43	0.339	0.239	0.0288
F1 (Rejet-de-Beaulieu)	Sandy clay	0.43	0.339	0.239	0.0288
F4 (Rejet-de-Beaulieu)	Loam clay-sand	0.398	0.255	0.148	0.1032
F (Mazinghien)	Clay loam	0.464	0.318	0.197	0.0552
F (Ors)	Flint clay	0.475	0.396	0.272	0.0144
F (Zarzuela)	Fill	0.437	0.091	0.033	5.04
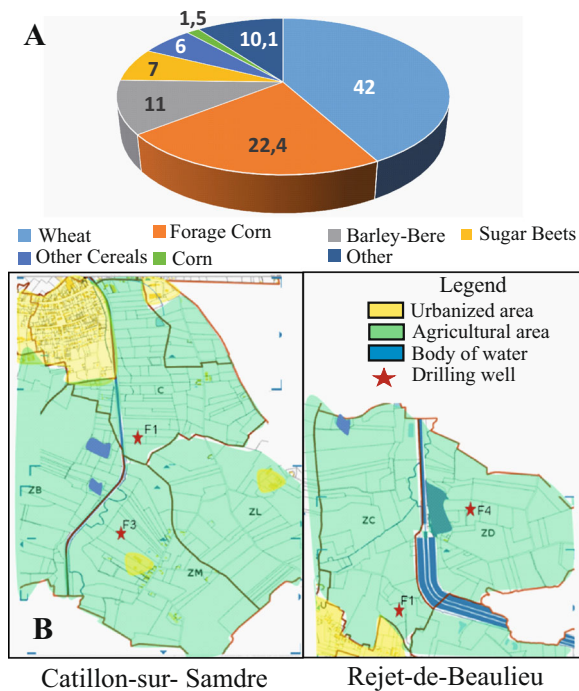
Fig. 3 Urbanized areas and agricultural zone

Between 1980 and 1990, it was considered that all agricultural areas were cultivated. From 1990 to 1998 and from 2000 to 2010, the plan of the soil occupation evolution was followed. Figure 4 shows the different concentrations calculated in each area.

For all areas, the nitrate concentrations from 1980 to 1990 are quite high in the root zone. During this period, the parcels were considered cultivated and the wheat crop occupies one rotation in two. In area 1 which represents the farmland surrounding the drilling F1 Catillon-sur-Sambre, concentrations reached in this decade, where the fertilizer supply was still considerable,

Table 5 Quantities of fertilizer applied to different crops

	Time	Doses made (kg/ha/year)
Wheat	1980–1990	220
	1991–2010	170
Corn	1980–1990	160
	1990–2010	140
Barley-Bere	1980–1990	200
	1990–2010	160
Sugar beets	1980–1990	160
	1990–2010	110

120 mg/l. Given the clayey nature of soils in this sector, becoming sandblasting at the bottom, the nitrates reside and accumulate in this slice of the soil before being leached. Area 2, which encompasses the land surrounding the drilling F3 in Catillon-sur-Sambre shows nitrate concentrations in the root area much lower than in other sectors. This result can be explained by the dominance of leafy land on cultivated land. The maximum concentration is from 26 mg/l. Areas 3 and 4, which represent respectively the lands surrounding F4 Rejet-de-Beaulieu and F1 Rejet-de-Beaulieu, reveal higher concentrations between 1980 and 1990. In the area 4 simulations, the barley-bere was the dominant crop.

From 1990, land use data have allowed to vary the simulations. Several agricultural parcels have been transformed to grasslands or forests. It explains the fall in nitrate concentration evolution. In area 1, concentrations decreased from 120 to 30 mg/l. However, there is a slight increase between 1999 and 2002, when precipitations have been abundant, and therefore, a refill in nitrates.

Since 2000, where cultivation practices have been taken back, we see a further increase of nitrate concentrations but with lower values compared to the 1980–1990 and this is probably due to the application of the policy of reasoned agriculture.

4.2 Unsaturated Zone (VS2DT)

The thickness of the unsaturated zone is important in the determination of the nitrates' transfer to the aquifer (Fig. 5). Beyond the thickness, the model was established by integrating the physical and hydraulic parameters of the different layers that constitute this horizon, as well as the precipitation that determines the flows (the same as for the root zone). The recharge water naturally contains nitrates, even without the use of fertilizers. These nitrates come mainly from the mineralization of humus and from rainwater. Studies conducted by Beckelynck et al. (1982) show that in rural areas, water contains 1.34 mg/l of nitrogen. In the same way, Foster et al. (1982) estimate that the recharge water of the aquifer under the forests contains 2 mg/l of nitrogen. The results from AgriFlux have been integrated into VS2DT to simulate the concentrations in the unsaturated zone. Figure 5 shows distribution of concentrations in the unsaturated zone at different time steps.
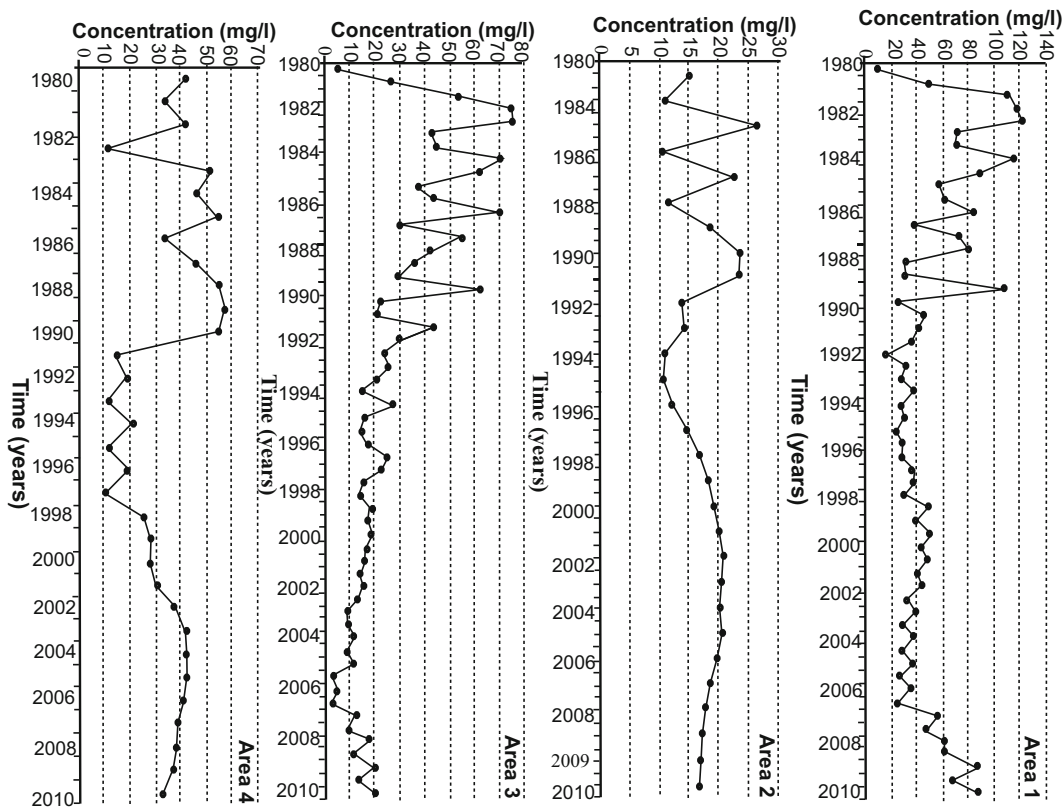
Fig. 4 Evolution of average nitrate concentrations in the root zone (zones 1, 2, 3, and 4)

From the first simulation (1980), the nitrates reach very quickly the bottom of the unsaturated zone in the sector of Bazuel and F1 Rejet-de-Beaulieu. In the first sector (Bazuel), the thickness of the unsaturated layer is low (5 m), then nitrates pass rapidly through this thickness.

In the second sector (F1 Rejet-de-Beaulieu), although the thickness of the unsaturated zone is higher, nitrate concentrations reach 17 mg/l. This is due to the nature of the unsaturated zone and the type of crop considered in the simulation (dominance of the wheat and barley-bere). Although we considered in this period that parcels were grown throughout the study area, nitrate concentrations remain low with a maximum of 17 mg/l. In 1985, nitrate concentrations are higher throughout the study area and it reached a maximum of 68 mg/l in sector F1 Catillon-sur-Sambre and La Groise (located at 2.5 km east of Catillon-sur-Sambre) (exceeding the drinking water requirements at 50 mg/l). The minimum of 17 mg/l is located at Mazinghien (located at 2.5 km west of

Rejet-de-Beaulieu), although it was at 1980 in the same sector of 9 mg/l.

Since 1990, through information about the evolution of land occupation between 1990 and 1998, many agricultural parcels have been transformed into prairie lands, hence the decrease in nitrate concentrations. This is the case of the F3 Catillon-sur-Sambre area, where concentrations decreased from 24 mg/l in 1985 to 19 mg/l in 1990 and from 67 to 43 mg/l (maximum) in sector F1 Catillon-sur-Sambre. In 1995, concentrations continued to decrease to reach a peak of 28 mg/l. This is not only due to the presence of prairie lands but also to the reduction of fertilizer quantities applied to the surface. The evolution of land use between 2000 and 2005 indicates return to crops. From 2000, we note that concentrations are increasing gradually throughout the study area in order to reach in 2010 a maximum of 66 mg/l in the sector of F1 Catillon-sur-Sambre. Despite the reasoned fertilization, the return to crops results in a rise of nitrate concentration. Then, it appears that in this area, the quality of groundwater is very sensitive to agricultural corps.
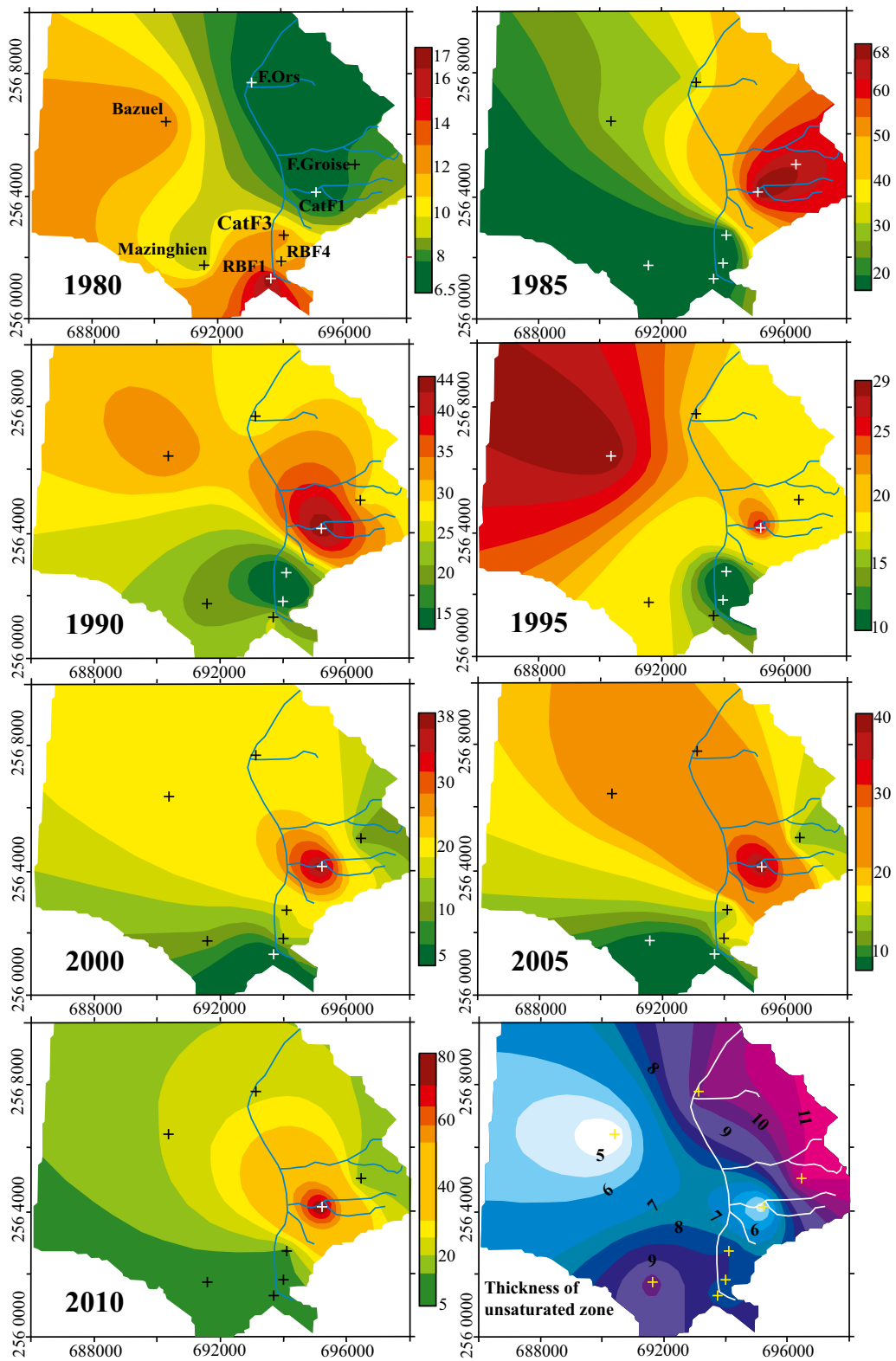
Fig. 5 Spatial and temporal distribution of nitrate concentrations in the unsaturated zone

4.3 Saturated Zone (ModFlow and MT3D)

The model is configured by dividing the aquifer into two layers and three horizons among which the first horizon (the upper layer) represents the topography of domain and the last represents the pace of the substratum. The domain of flow is discretized in square stitches of 100 m aside. Before attaining the stage of simulation of the diffusion of nitrates in groundwater, the hydrodynamic model was established. This stage starts with the definition of geometry of aquifer following the model calibration. The pumping flow, geometry of aquifer, and hydraulic conductivity were used for the calibration of hydrodynamic model, which was based on the piezometric of year 1982 for calibration in permanent regime. The calibration of the piezometry was accomplished on a step of time of 180 days over a period of 28 years (1982–2010) (Fig. 6).

Figure 7 shows an example of the good superimposing of piezometric levels measured and calculated in the drilling well F1 Catillon-sur-Sambre in transient modeling.
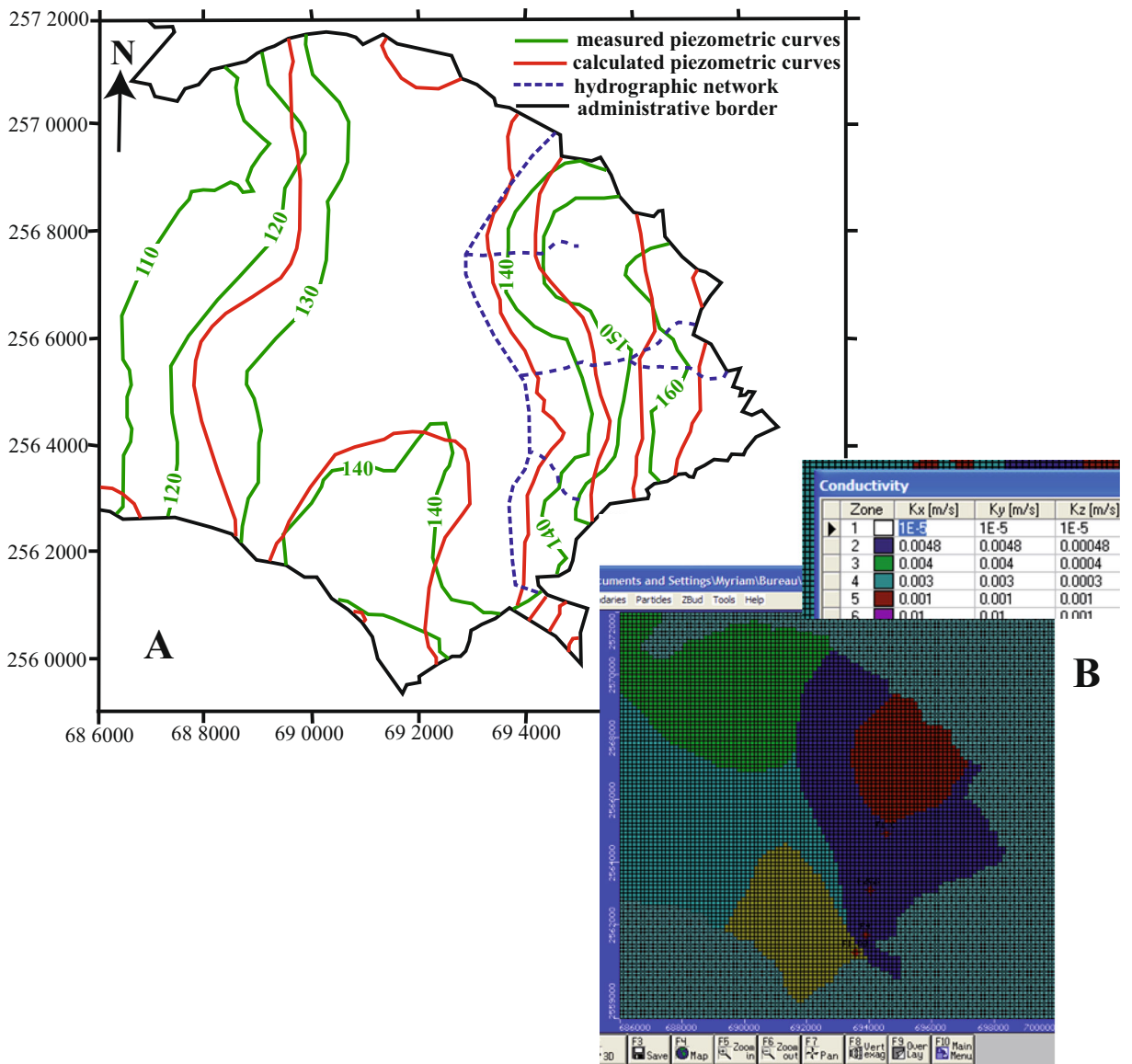
Fig. 6 Comparison between measured piezometric contours and computed contours (**a**). Spatial distribution hydraulic conductivity (**b**)
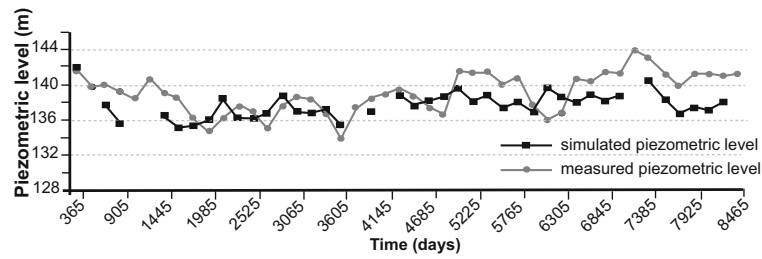
Fig. 7 Comparison of piezometric levels measured and calculated in transient modeling

Concentration in nitrates got by simulation in the unsaturated zone was introduced into the model MT3D as recharge to model concentration in nitrate in groundwater. Hydrodispersive modeling was based on the calibration of the parameter of dispersion which was considered of the order of 20 m. Results coming from this modeling show a good correlation between measured and predicted nitrate concentration. Figure 8 illustrates an example of results got for drilling wells F1 Catillon-Sur-Sambre and F1 Rejet-De-Beaulieu.

4.4 Forecasts

The groundwater quality in the study area, beyond the rainfall, geological nature, and influence of the fertilization applied to the surface, it remains very sensitive to applied crop type. Therefore, the absence of cultures by a return to the grassland is followed by a fall of nitrates in waters of drilling wells. On the contrary, the installation of cultures, and especially the wheat, increases nitrate concentration. To assess this influence and to determine an optimum scenario allowing reconciling agricultural
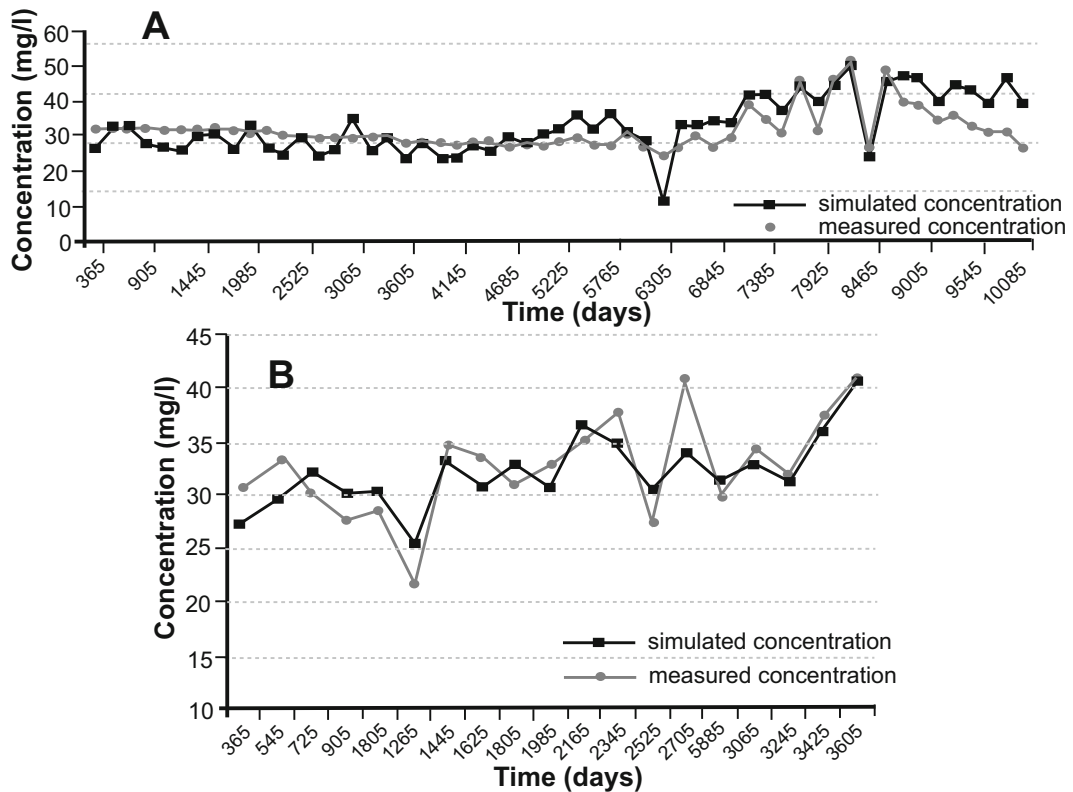
Fig. 8 Comparison of concentration in nitrates measured and calculated in the groundwater (**a** Catillon-sur-Sambre, **b** Rejet-de-Beaulieu)

activity and maintaining of a drinking water ($[NO_3^-]$ < 50 mg/l), two scenarios of prediction of concentration in nitrates were envisaged from 2015 until 2035.

The first scenario consists in estimating concentration of the soil towards the groundwater by considering that all region of study is cultivated during 20 years of simulation.

In the second scenario, no culture was considered, and fair contributions in nitrogen necessary for the grasslands were introduced as given.

In these configurations, the precipitation simulations were carried out based on the HydriFlux model in AgriFlux. This model makes it possible to simulate rainfall in a probabilistic statistical manner requiring the 12 values of average monthly precipitation and the number of precipitation days per year.

Concentration in nitrates, which attain the groundwater, in the case of an intense culture, is very high in comparison with the present state where some agricultural plots are cultivated and others stay under grasslands. In the case of simulation according to scenario I (all agricultural plots are cultivated) concentration passes of a maximum value of 32 mg/l (F4 Rejet-de-Beaulieu) to 48.48 mg/l. It is also the case for other drilling wells. The highest concentration characterizes the drilling well F1 Catillon-sur-Sambre where stocks pass from 50 mg/l in varied culture to 85.21 mg/l in the case of scenario I (Fig. 9). On the other hand, simulation in scenario II considered that all agricultural plots were in grasslands which cause considerable reduction of nitrate concentrations in the groundwater which reaches a maximum of 15 mg/l.

The case of bringing under cultivation of the drilling well F1 Catillon-sur-Sambre, which gives concentrations exceeding the drinking water limit by dint of a
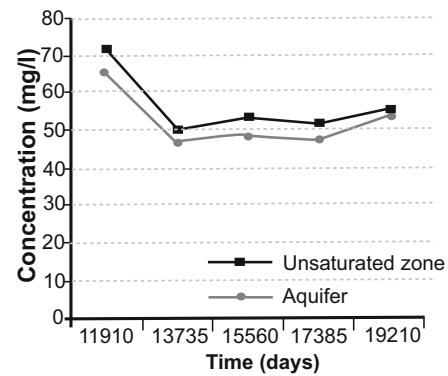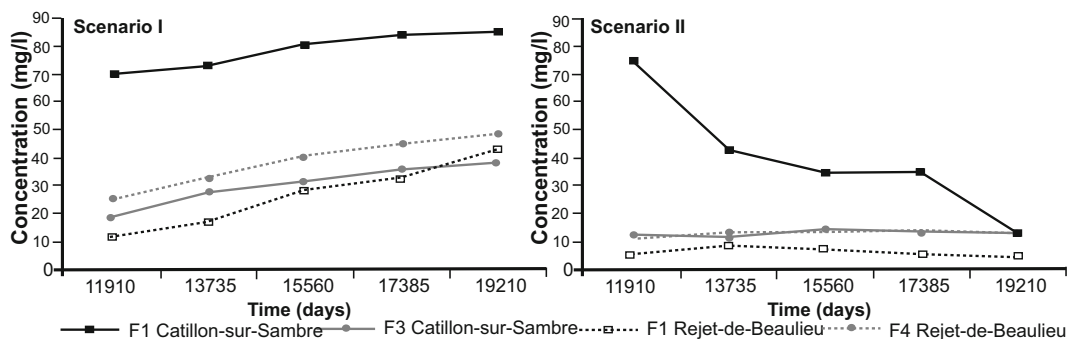
Fig. 10 Evolution nitrate concentration in the unsaturated zone and in the groundwater in drilling well F1 Catillon-sur-Sambre: use of the cultures of sugar beets

quick transfer of the nitrogenous fluxes, made the object of simulation consider different cultures. So, additional simulation has been accomplished on this catchment by considering only the single culture, that of sugar beets that does not ask for big nitrogen quantity. The results of nitrate concentration obtained (Fig. 10) at the level of the groundwater are close to the drinking water requirements (50 mg/l). By combining this scenario with the transformation into grassland at the end of 20 years, drilling well finds concentration close to the threshold of potability.

To attain lower concentrations relative at water drinking limit, the simulations considered the annual alternations of sugar beet grassland (at the end of the culture of sugar beets, they transform into grassland until new cultivation). Results obtained (Fig. 11) show concentration, this time, always lower than the drinking water quality.

Other scenarios can be used to find adequate conditions to exploit properly drilling well F1 Catillon-sur-Sambre without becoming restricted in the only culture of sugar beets. These solutions represent a space

Fig. 9 Evolution of nitrate concentration in the saturated zone according to the scenarios of predictions
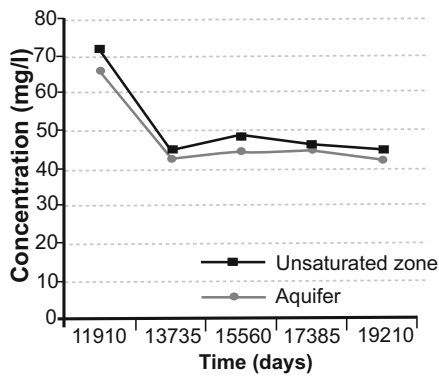
Fig. 11 Evolution of nitrate concentrations in the unsaturated zone and in the groundwater in drilling well F1 Catillon-sur-Sambre: use of alternations sugar beet grasslands

division differentiated from various cultures. To find the good sharing out of areas to be cultivated according to the crop type, the model which was developed in this study attained its limits. This work will be the subject of a further study.

5 Conclusion

This paper included an analysis, within the European laws in the water quality field (2000/60/EC), of the impact of agriculture and the urban nitrogen load on the groundwater quality in the sector (Catillon-sur-Sambre and Rejet-de-Beaulieu) in the North of France. Agriculture caused an important deterioration of the water quality in this sector. To understand the impact of agricultural activity on the quality of the water table, we have put in place an integrated model (AgriFlux-VS2DT-ModFlow-MT3D) which makes it possible to simulate the transformation and the transfer of nitrates from the surface to the water table.

The first results show that a considerable decrease of medium concentration in nitrates attaining the base of the unsaturated zone was proved. This concentration passed 68 mg/l in 1985 to 30 mg/l in 2010, except for the sector of the drilling well F1 Catillon-sur-Sambre, marked by a thickness of the weak unsaturated zone, where even in 2010, concentration remains high.

Nitrate concentration in the groundwater fluctuates strongly but do not exceed 40 mg/l in the drilling wells F3 Catillon-sur-Sambre and F1–F4 Rejet-de-Beaulieu. The drilling well F1 Catillon-sur-Sambre introduces once again strong concentration in nitrates, which attain 55 mg/l.

Two scenarios have been envisaged for a prediction over 20 years: zones completely cultivated or transformed into grasslands. He comes out again from this projected simulation of strong concentration in the groundwater in the case of scenario I. On the contrary, when plots are not cultivated, concentration in nitrates in the aquifer remains very low. It follows that nitrate concentration in the aquifer is closely linked to cultural practices as well as quantity manure used and to a lesser degree in the characteristics of the soil (nature of the soil and thickness of the unsaturated zone).

To face the problems met by the administrators, a reasoned management is obviously accompanied with rotations of cultures and of transformations into grassland. So, for the sectors of drilling well F3 Catillon-sur-Sambre and F1–F4 Rejet-de-Beaulieu, a transformation into grassland is obvious every 20 years without requirement on rotations of cultures. On the contrary, drilling well F1 Catillon-sur-Sambre, considering its sensitivity in contribution in nitrates by cultures, it is necessary to use cultures producing least nitrogenous fluxes of type sugar beets. It should be accompanied by transformations into a grassland in lower length than the previous ones, specifically 15 years. To make sure of the working permanence of this drilling well, an alternation annual sugar beet grassland is also obvious. Other solutions can be envisaged as part of a supplementary work; for example, it is the case of a space division differentiated from cultures.

The model makes it possible to correctly evaluate the concentrations of nitrates reaching the groundwater with a monitoring of the concentration evolution in each lithological horizon, thus constituting a good tool for the management of agricultural pollution.

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