Modelling the effect of physical and chemical characteristics of shallow aquifers on water and nitrate transport in small agricultural catchments


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Abstract

The aim of this study is threefold: (1) to evaluate the effect of the physical properties of weathered granitic material (geometry and spatial distribution of hydraulic conductivity) on water fluxes at the outlets of two small and nearby agricultural catchments, Kerbernez and Kerrien (0.12 and 0.095 km²), underlain by granite bedrock; (2) to explain the variations of nitrate concentration in streamwater in relation to the spatial distribution of dissolved nitrate in the groundwater; (3) to investigate the origin of the groundwater nitrate by analysing the reaction times of groundwater to variations of nitrate concentration in water recharge. These objectives were attained by developing a flow and nitrate transport model for the two catchments from geophysical measurements on the geometry and hydraulic conductivity of the weathered granite layer, and using data collected from soil surveys. The models were calibrated and validated from spatial and temporal observations of hydraulic heads and nitrate concentrations in groundwater and stream water. The flow models appeared to be less sensitive to the geometry of the weathered granite layer than the spatial distribution of hydraulic conductivity. Model results show that seasonal patterns of nitrate concentrations in streamwater result partly from the spatial distribution of nitrate concentration in the groundwater. The horizontal distribution of nitrate concentrations in groundwater derives from denitrification in the downslope domain. An analysis of the groundwater reaction times for both catchments shows that, following a variation in the recharge nitrate concentration; the time to reach equilibrium in the whole groundwater body is more than 14 years. In the Kerbernez catchment, the vertical distribution observed in groundwater nitrate concentrations appears to be caused by a temporal decrease of the nitrate concentration in the water recharge over the last 15 years.

Keywords: Agricultural catchments; Weathered granite; Flow and transport models; Groundwater response time; Nitrate; Stream concentration

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1. Introduction

In intensive agricultural catchments on weakly permeable or impervious bedrock, shallow groundwaters developing in the weathered bedrock material often constitute an important reservoir of nitrate (Bohlke and Denver, 1995; Steinheimer and Scoggin, 1998; Ruiz et al., 2002b). The key role of the shallow groundwater in stream nitrate exportation from catchments has been clearly demonstrated by relating seasonal variations of streamwater nitrate concentrations to variations of the water-table (Schnabel et al., 1993; Creed and Band, 1998; Molénat et al., 2002). However, there can be numerous mechanisms behind this relationship. Creed and Band (1998) propose the flushing hypothesis, in which the rising water table flushes the nitrate from the top soil layer into the stream. Molénat et al. (2002) consider that the stream concentration variations may be attributed to the mixing of three end-members in groundwater, whose contributions vary with time depending on water-table depth. Moreover, biotransformations such as het erotrophic denitrification in riparian areas also influence streamwater nitrate concentrations (Altman and Parizek, 1995; Hill, 1996).

Mechanisms controlling nitrate exportation from a catchment depend on topographic, lithological, pedological and climatic conditions. Their identification and quantification cannot be based solely on the analysis of the nitrate concentrations variations in stream water. Local and distributed observations of water chemistry, as well as the intrinsic catchment properties, can be used to constrain conceptual models that are able to represent patterns of stream water concentration. In particular, we need to stress the effect of the physical and chemical characteristics of shallow groundwater on nitrate transport. Some local information is provided by well boring (water-table levels, concentrations, hydrodynamic properties) (Modica et al., 1998; Trabada-Crende and Vinten, 1998; Puckett and Cowdery, 2002), while global methods such as geophysics reveal the spatial heterogeneities in physical or chemical properties of shallow groundwater that can modify water and nitrate transport (Tabbagh et al., 2000; Garambois et al., 2002; Sandberg et al., 2002). The combination of local and global methods provides an interesting approach, along with modelling, to improve our knowledge of water and solute transport processes in catchments.

This paper presents a comprehensive field study on water and nitrate transport in two neighbouring catchments in western France, the Kerbernez and Kerrien catchments. The field study aimed at understanding the mechanisms underlying the nitrate exports by streams in catchments on weakly permeable or impervious bedrock with shallow groundwater (Martin et al., 2004). The two catchments have been surveyed extensively by hydrological, hydrochemical, hydrogeological and geophysical approaches. These surveys allow the collection of data on intrinsic catchment properties such as the geometry and the hydraulic characteristics of the soil and geological formations. In addition, nitrate concentrations and water-table depths have been determined in groundwaters using a large number of piezometers. Meanwhile, stream discharge and stream nitrate concentrations have been recorded over a period of 2 years. Various assumptions have been proposed about nitrate export mechanisms from the catchment. The variations in stream water concentrations appear to be derived mainly from the spatial pattern of nitrate concentration in groundwater and not from the temporal variations of nitrate leaching in soil (Martin et al., 2004).

The aim of this study is threefold: (i) to evaluate the effect of the physical properties of weathered granitic material (geometry and spatial distribution of hydraulic conductivity) on water fluxes at the outlets of the Kerrien and Kerbernez catchments, (2) to explain the nitrate concentration variations in the streamwater in regard to the spatial distribution of nitrate concentrations in the groundwater, and (3) to investigate the origin of the nitrate concentration distribution in the groundwater from analysing groundwater reaction times in relation to variations of nitrate concentration in the water recharge.

2. Materials and methods

2.1. Site description

Kerbernez (0.12 km$^2$) and Kerrien (0.095 km$^2$) are two adjacent nearby first-order catchments located in South Western Brittany (France) (47°57'N—4°8'W) (Fig. 1). They have been
Fig. 1. Study site location: piezometer positions, surface slopes and geological cross-section along the AB profile, inferred from geophysical measurements in the Kerbernez and Kerrien catchments (adapted from Legchenko et al. (2004)).
previously described by Ruiz et al. (2002a); Martin et al. (2004). The Kerbernez and Kerrien catchments have variable contributing areas in the sense that most of the surface runoff is observed only in the bottom land along the stream reach where the water-table is very close to or at the soil surface. Surface runoff is never observed on the upper slope where the soils are unsaturated. All the rainfall infiltrates the soil down to the groundwater.

Climate is oceanic, with a mean annual precipitation and potential evapotranspiration (calculated for the last decade) of 1185 and 620 mm, respectively.

Land use is mainly agricultural. Most arable fields (43% of cultivated land area), which grow maize and cereals alternatively, are farmed intensively involving importation of pig slurry and cattle manure. Most of the grasslands (40% of the cultivated area) are intensively grazed by dairy cows (Ruiz et al., 2002a).

Elevations range from 40 m in upslope parts of the catchments to 13 m at catchment outlets. Slope profiles are also different between the two catchments, being convex for Kerbernez (gradients varying from 5% upslope to 8% downslope) and concave for Kerrien (gradients varying from 14% upslope to 5% downslope) (Fig. 1).

The bedrock is made up of granite, overlain by weathered granitic material having a mean thickness of about 20 m. Geophysical surveys (electrical imaging, electromagnetic and Magnetic Resonance Sounding—MRS) indicate that the thickness of the weathered granitic material increases from upslope towards downslope parts of the catchments, in the form of a deep graben structure (Fig. 1) (Legchenko et al., 2004). Soils are mainly sandy loam, on average 1 m deep. Soils are well drained, except in the relatively narrow bottom lands where hydromorphic soils are found. Pumping tests (Vouillamoz, 2003) and MRS measurements (Legchenko et al., 2004) have shown that the hydraulic conductivity in the weathered granite layer (WGL) ranges from $2 \cdot 10^{-6}$ to $5 \cdot 10^{-4}$ m s$^{-1}$ (Table 1). The saturated hydraulic conductivity of the soil is around $5 \cdot 10^{-4}$ m s$^{-1}$ (Lamandé, 2003).

The two catchments show contrasting temporal patterns of streamwater nitrate concentrations. In the Kerrien catchment, streamwater nitrate concentrations are high during the rainy season in winter and decrease in summer and autumn. In Kerbernez, streamwater nitrate concentrations follow an inverse pattern compared with Kerrien, with lower concentrations in winter and the higher in summer. According to Martin et al. (2004), the winter concentration peak in the Kerrien catchment would correspond to the peak in discharge of nitrate-rich shallow groundwater towards the stream. In summer, this discharge would decrease in comparison to the input from the denitrified stream riparian zone. In the Kerbernez catchment, the inverse pattern would result from stratification in the groundwater chemistry. The contribution of the deeper layer would increase in summer, the nitrate concentrations being higher in the deeper than in the shallower layer. Moreover, the difference in stream nitrate concentration between the two catchments could also result from an extension of the stream riparian zone where denitrification processes are occurring. In Kerbernez, the riparian zone is much more restricted than in the Kerrien catchment (Martin et al., 2004).

2.2. The hydrological data

The studied period extended from 1st September 2001 to 31st August 2002. The amount of precipitation during this period reached 987 mm, with a potential evapotranspiration (PET) of 733 mm. The specific discharges were similar for the two catchments, with 197 and 181 mm for Kerbernez and Kerrien, respectively. Peaks of discharge occurred in winter. Stream flow remained relatively high during summer for the Kerbernez catchment, whereas the Kerrien catchment stream almost dried up in late summer and autumn. The two catchments were equipped with a set of piezometers, with depths ranging from 5 to 20 m (Fig. 2). Water-table levels were automatically recorded with a 15-min time step at 6 piezometers (B5B-B4-A1B and F5B-F4-F1B) arranged from upslope to downslope in the two catchments. For the two catchments, annual variations of the water table in upslope domains ranged from about 4 m depth in winter down to 8 m depth in summer. In the downslope domains, annual variations of the water table were less than 1 m for both catchments, remaining close to the ground surface.
3. Model rational and parameterisation

The three-dimensional groundwater movement is represented by the following partial differential Eq. (1):

\[
\frac{\partial}{\partial x} \left( K_i e \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial y} \left( K_j e \frac{\partial h}{\partial y} \right) + \frac{\partial}{\partial z} \left( K_z e \frac{\partial h}{\partial z} \right) \\
\pm W(x, y, z, t) \\
= S \frac{\partial h}{\partial t}
\]

where \( h \) is the hydraulic head and \( e \) is the groundwater thickness, \( S \) corresponds to the specific yield for surface free groundwater and specific storage for confined groundwater, while \( K_i \) is the hydraulic conductivity in direction \( i \) and \( W \) represents the source or sink fluxes per unit surface area. In our case, the source and sink correspond to the water recharge from soil and the stream discharge, respectively. Numerical solutions of Eq. (1) were computed using the MODFLOW code (McDonald et al., 1988) by means of the finite-difference method.

Nitrate transport in the groundwater is represented by the convection, diffusion and dispersion Eq. (2), which was solved by MT3D (Zheng, 1990) and expressed in its general form as (de Marsily, 1981):

\[
\text{div}(\overline{D} \text{grad}(C) - C \vec{U}) = \omega_c \frac{\partial C}{\partial t} + (\omega_t - \omega_c) \frac{\partial C'}{\partial t}
\]

where \( \overline{D} \) represents the hydrodynamic dispersion tensor, \( C \) and \( C' \) are the solute concentrations in the mobile and immobile fraction, respectively, \( \omega_c \) is the total porosity, \( \omega_c \) is the effective porosity and \( \vec{U} \) the Darcy flow, calculated from hydraulic heads simulated by MODFLOW.

Table 1

Hydrodynamic properties of the soil and the weathered granitic layer: \( K \) the saturated hydraulic conductivity (m s\(^{-1}\)), \( T \) the transmissivity (m\(^2\) s\(^{-1}\)), \( S_y \) the specific yield, \( S_s \) the specific storage and \( u_t \) the total porosity

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>( 5 \times 10^{-4} )</td>
<td>Infiltrimetry(^a)</td>
</tr>
<tr>
<td>( S_y )</td>
<td>0.2</td>
<td>Retention curves(^b)</td>
</tr>
<tr>
<td>( u_t )</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Weathered granitic layer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kerbernez</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B5B</td>
<td>K</td>
<td>( 5 \times 10^{-6} )</td>
</tr>
<tr>
<td></td>
<td>T</td>
<td>( 2 \times 10^{-6} )</td>
</tr>
<tr>
<td>Midslope (B4)</td>
<td>K</td>
<td>( 5 \times 10^{-5} )</td>
</tr>
<tr>
<td></td>
<td>T</td>
<td>( 3 \times 10^{-5} )</td>
</tr>
<tr>
<td>Downslop (A1B)</td>
<td>K</td>
<td>( 5 \times 10^{-4} )</td>
</tr>
<tr>
<td>Kerrien</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F5B</td>
<td>K</td>
<td>( 9 \times 10^{-6} )</td>
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<tr>
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<td>( 2 \times 10^{-4} )</td>
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<td>Midslope (F4)</td>
<td>K</td>
<td>( 3 \times 10^{-5} )</td>
</tr>
<tr>
<td></td>
<td>T</td>
<td>( 2 \times 10^{-5} )</td>
</tr>
<tr>
<td>Downslop (F1B)</td>
<td>K</td>
<td>( 5 \times 10^{-4} )</td>
</tr>
<tr>
<td></td>
<td>T</td>
<td>( 7 \times 10^{-4} )</td>
</tr>
<tr>
<td>The two catchments</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( S_s )</td>
<td>( 3 \times 10^{-4} )</td>
</tr>
<tr>
<td></td>
<td>( u_t )</td>
<td>( 0.60 )</td>
</tr>
<tr>
<td></td>
<td>( S_y )</td>
<td>( 0.05 )</td>
</tr>
</tbody>
</table>

\(^a\) Lamandé (2003).  
\(^b\) Widiatmaka (1994).  
\(^c\) Legchenko et al. (2004).  
\(^d\) Vouillamoz (2003).
3.1. Flow model parameters and model geometry

The model was divided into three layers, comprising the soil, with a thickness of 1.50 m, the WGL and the low permeable bedrock, with the basal limit fixed at −30 m below sea level. The soil surface elevation was derived from the Digital Elevation Model (DEM) for the catchments. The DEM was built up from a topographic survey, with a grid size ranging from 5 to 20 m depending on the catchment zones. In both catchments, the free groundwater surface is contained in the soil and in the weathered granite layer (WGL) depending on the location. The specific yield needed to be fixed for both materials. For the soil layer, it was fixed at 20%. This corresponds to the difference between the soil moisture at saturation and at field capacity (pF 2.0) as measured by Lamandé (2003). The specific yield for the WGL was derived from an analysis of the water-table depth variation following rainfall (Fig. 3). The specific yield was estimated as the ratio between variations in infiltration and water table depth measured at the beginning and the end of the event. The infiltration was taken as the effective rainfall, which is defined as the difference between the precipitation $P$ and the potential evapotranspiration $PET$ during the event. For the two catchments, the calculation gave a value of around 10%. The specific yield was also estimated through geophysical
measurements (MRS), yielding values around 5% (Legchenko et al., 2004). The specific storage values were attributed to the WGL and the bedrock from pumping tests (Vouillamoz, 2003). An analysis of the tests shows that the WGL has an average value of $3 \times 10^{-4}$. This value was extrapolated to the bedrock. The hydraulic conductivity values were adjusted using an approach reported in the calibration section.

Simulations were expected to be very sensitive to the spatial distribution of the hydraulic conductivity and the WGL thickness. Considering the few data available, it was difficult to interpolate between the values obtained from pumping test performed in piezometers and from the thickness estimation derived from the geophysical survey. We first chose to test different WGL geometries and then different spatial distributions of the hydraulic conductivity. While all the models (Fig. 4) were quite simple, they were always in agreement with the observations. Firstly, we compared a model with a uniform WGL thickness of 20 m (case G1) to a model with variable WGL thickness between the upslope (20 m) and downslope (30 m) (case G2). The case G2 was drawn directly from the geophysical survey (Fig. 1) (Legchenko et al., 2004). For both of these cases, the values of hydraulic conductivity were considered uniform in space, being estimated from field measurements. Secondly, we evaluated the effect of the spatial distribution of hydraulic conductivity on hydraulic head and water flux at the catchment outlets. A model with a horizontal gradient of hydraulic conductivity (case K1) was compared against a model with a vertical gradient of hydraulic conductivity (case K2) (Fig. 4, Table 2). For these two
configurations, the thickness of the WGL remained constant (20 m) and the values of hydraulic conductivity were adjusted from field measurements and calibrated against stream discharge and hydraulic head observations.

In all the models evaluated here, the bedrock was considered as a very weakly permeable layer with a hydraulic conductivity of $1 \times 10^{-9}$ m s$^{-1}$.

### 3.2. Transport model parameters

The molecular diffusion was considered to be negligible. The dispersion was related to the water velocity by the dispersivity parameter. The dispersivity was fixed at 10 m based on the dependence relation between scale and dispersivity reported in the literature (Gelhar et al., 1992).

The transport model depended on the total porosity and the effective porosity of the porous materials. The total porosity of the soil and WGL was attributed following the data of Lamandé (2003); Widiatmaka (1994). The effective porosity for the soil was taken as the specific yield determined as explained in Section 3.2. For the WGL, the effective porosity was fixed at 8% corresponding to the mean values between specific yields estimated by the analysis of the water-table variation and measured by MRS. All the values of effective and total porosity are listed in Table 1.

<table>
<thead>
<tr>
<th>Flow domain</th>
<th>Domains</th>
<th>Kerbernez</th>
<th>Kerrien</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>–</td>
<td>3 × 10$^{-6}$</td>
<td>7 × 10$^{-6}$</td>
</tr>
<tr>
<td></td>
<td>Up slope</td>
<td>3 × 10$^{-6}$</td>
<td>5 × 10$^{-7}$</td>
</tr>
<tr>
<td>K1</td>
<td>Midslope</td>
<td>5 × 10$^{-6}$</td>
<td>7 × 10$^{-6}$</td>
</tr>
<tr>
<td></td>
<td>Downslope</td>
<td>5 × 10$^{-3}$</td>
<td>5 × 10$^{-4}$</td>
</tr>
<tr>
<td>K2</td>
<td>WGA shallower part</td>
<td>5 × 10$^{-6}$</td>
<td>1 × 10$^{-5}$</td>
</tr>
<tr>
<td></td>
<td>WGA deeper part</td>
<td>5 × 10$^{-7}$</td>
<td>1 × 10$^{-6}$</td>
</tr>
</tbody>
</table>

### 3.3. Spatial discretisation and boundary conditions for flow and transport models

The lateral groundwater flow boundary was assumed to be similar to the topographic catchment boundary. In the Kerbernez and Kerrien catchments, as well as in other catchments of the Brittany region (Wyns, 1998), this assumption appears realistic because the groundwater surface as measured from the piezometer network follows the soil surface. We considered a zero water flow along the lateral groundwater boundary. Topographic catchment boundaries were delineated from the DEM. Grid size ranged from 5 m in the downslope domain to 20 m in the upslope domain where the slope was smoother.

Flow model boundary conditions were set by the water level in the stream reach and by the water recharge occurring over the free surface groundwater. The stream reach was modelled as a drain in which the water level was fixed. The groundwater was assumed to discharge into the stream when the hydraulic head along the stream was higher than the drain water level. In the present study, the use of a drain boundary condition to model streamflow is justified by the small size of the river bed, the width of the stream channel being less than 1 m. Daily groundwater recharge rate was calculated from daily rainfall and PET measurements, considering that the soil acted as a reservoir in which the initial water deficit controlled infiltration of the effective rainfall. For the 2001–2002 hydrological year, there was an initial soil water deficit of 125 mm at the end of summer period. The annual cumulative groundwater recharge was then 299 mm.

Transport model boundary conditions were defined by the nitrate concentration in the recharge water. These concentrations were associated with the nitrate concentration due to soil leaching, which was computed from the Burns model as a function of the nitrate stock in the soil and the daily water drainage. To represent the soil nitrate stock, the Burns model takes account of the soil organic input and output from agricultural practices and the nitrogen cycle processes in the soil (Burns, 1974). A daily nitrate concentration was assigned to each daily water recharge (Fig. 5). To take account of the transfer time into the soil, the nitrate concentration in the recharge water was calculated from the nitrogen excess and the annual drainage of the year preceding the studied period. In 2000–2001, the nitrogen excess for Kerbernez and Kerrien was, respectively, 83 and 70 kg N ha$^{-1}$ y$^{-1}$, while the amount of drainage water was 601 and 614 mm, respectively. This corresponds to mean
nitrate concentrations in the recharge water of 61 and 50 mg l\(^{-1}\) for the Kerbernez and Kerrien catchments, respectively. To analyse the role of time variability in the nitrate concentration of the recharge, we also ran simulations with a constant concentration in the groundwater recharge over a period equal to the mean annual concentration. Considering the large uncertainties in the nitrogen budget calculations (Ruiz et al., 2002a), a value of 60 mg l\(^{-1}\) was attributed as the mean nitrate concentration in the recharge water of the two catchments.

3.4. Initial conditions and denitrification processes in transport model

Initial nitrate concentrations in the groundwater were fixed from analyses performed on the groundwater (Martin et al., 2004) (Fig. 2). Observations showed that the Kerbernez catchment groundwater was stratified, with a vertical gradient of nitrate concentrations ranging from 60 mg l\(^{-1}\) below the groundwater surface to 80 mg l\(^{-1}\) at a depth of approximately 20 m. Following these observations, the model for the Kerbernez groundwater was divided into two 10-m thick layers according to initial nitrate concentrations. Values of 60 and 80 mg l\(^{-1}\) were attributed to the upper and the lower layer, respectively. In the Kerrien catchment, groundwater nitrate appeared to be almost uniform, with values around 60 mg l\(^{-1}\) (Fig. 2). This value was applied as the initial nitrate concentration of all the groundwater.

In both catchments, denitrification took place in the downslope domains of the groundwater body along the stream (Martin et al., 2004). Consequently, we simulated denitrification processes in these domains using a first-order irreversible decay, with a coefficient of 0.05 d\(^{-1}\), which corresponds to a half-life of 20 days (Flynn et al., 1999; Gardner et al., 2000). The extension of the denitrifying zone was mapped in the two catchments by electromagnetic surveys. All zones with an apparent conductivity less than 3 mS m\(^{-1}\) were considered as denitrifying zones. In this way, denitrifying zones extended over 0.5% of the catchment area for Kerbernez and over 2.5–5% for Kerrien. The vertical extension of denitrification processes was limited to the soil layer in the Kerbernez catchment, whereas it reached a depth of 10 m beneath the soil surface in the Kerrien catchment.

3.5. Calibration and validation procedures

The calibration of the flow model involved adjusting the hydraulic conductivities. This was carried out by a manual trial and error procedure, and considering the goodness of fit, \(d\), as the mean absolute difference between observed and simulated daily hydraulic heads. The calibration period ran from 01 September 2001 (day 1) to 31 August 2002 (day 365), preceded by a 30-day warm up period. For each catchment, the validation was performed on 3-month periods from 1st September 2002 to 30th November 2002.

Transport models were run three times in continuation, using the hydrological conditions and nitrate concentrations of the recharge water for the 2001–2002 hydrological year. Then, annual variations of stream nitrate concentrations were compared with observations for the year 2001–2002.

4. Results

4.1. Effect of WGL thickness on the flow model

The effect of the WGL thickness on the flow model was estimated by comparing the simulations with the...
G1 and G2 flow models. For each catchment, these differences were estimated in the upslope, midslope and downslope domains using two indices: $\Delta$, which is the mean value of the absolute difference between daily hydraulic heads simulated over the period with G1 and G2 flow models, and $\zeta$, which corresponds to:

$$\zeta = \frac{\Delta}{H_{\text{max}} - H_{\text{min}}}$$  \hspace{1cm} (3)

where $H_{\text{max}}$ and $H_{\text{min}}$ are the highest and the lowest water-table levels simulated during the period.

The WGL thickness variation had a moderate effect on the hydraulic head variations along the hillslope (Table 3). The main differences between the G1 and G2 flow models concern the downslope domain of the Kerbernez catchment ($\Delta = 0.49$ m) and the midslope domain of the Kerrien catchment ($\Delta = 0.48$ m). In the upslope domains of the two catchments, the differences between the two models were very slight.

This analysis shows that better simulations of hydraulic heads could not be obtained by taking into account the deep graben structure identified by geophysical investigations in the downslope domain of the two catchments. Consequently, further simulations were performed using a uniform flow model geometry (case G1).

### 4.2. Effect of spatial distribution of hydraulic conductivity on the flow model

#### 4.2.1. Water-table elevations

In the Kerrien catchment, the flow model performance was different depending on the spatial distribution of hydraulic conductivity (G1, K1 and K2), as assessed by the value of $\delta$, which is the mean absolute difference between observed and simulated hydraulic heads (Table 4). The uniform (G1) and stratified (K2) distributions led to great differences between simulations and observations, particularly in the upslope ($\delta = 4.04$ and 1.85 m in the case of G1 and K2, respectively) and midslope domains ($\delta = 2.92$ and 2.26 m in the case of G1 and K2, respectively). Simulations with the K1 distribution gave realistic hydraulic heads in the downslope ($\delta = 0.46$ m) and midslope ($\delta = 0.25$ m) domains. However, the K1 distribution resulted in a misfit in the upslope domain since the mean absolute difference between simulated and observed hydraulic heads remained at 3.67 m.

### Table 3

Mean absolute difference ($\Delta$) between hydraulic heads simulated following G1 and G2 configurations in upslope, midslope and downslope domains, and mean ratio ($\zeta$) between $\delta$ and difference between the highest and the lowest water table levels simulated during the period

<table>
<thead>
<tr>
<th>Flow model comparison</th>
<th>Catchment</th>
<th>Domain</th>
<th>Wells</th>
<th>$\Delta$ (m)</th>
<th>$\zeta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1/G2</td>
<td>Kerbernez</td>
<td>Upslope</td>
<td>B5B</td>
<td>0.01</td>
<td>0.31</td>
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<td></td>
<td></td>
<td>Midslope</td>
<td>B4</td>
<td>0.14</td>
<td>3.82</td>
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<td>A1B</td>
<td>0.49</td>
<td>21.82</td>
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<td></td>
<td>Kerrien</td>
<td>Upslope</td>
<td>F5B</td>
<td>0.26</td>
<td>4.93</td>
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<tr>
<td></td>
<td></td>
<td>Midslope</td>
<td>F4</td>
<td>0.48</td>
<td>14.51</td>
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<tr>
<td></td>
<td></td>
<td>Downslope</td>
<td>F1B</td>
<td>0.01</td>
<td>4.30</td>
</tr>
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</table>

### Table 4

Mean absolute difference ($\delta$) between measured and simulated hydraulic heads from G1, K1 and K2 configurations in upslope, midslope and downslope domains

<table>
<thead>
<tr>
<th>Flow model comparison</th>
<th>Catchment</th>
<th>Domain</th>
<th>Wells</th>
<th>$\delta$ (m)</th>
</tr>
</thead>
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<td>1.24</td>
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This discrepancy was constant in time, implying that there was a systematic gap between observed and simulated hydraulic heads (Fig. 6).

In the Kerbernez catchment, the best fit was also given by the K1 spatial distribution, even if differences between the three flow models were less important than in the Kerrien catchment (Table 4).

Since the K1 spatial distribution yielded the best fit in terms of hydraulic head simulation, this distribution was used to run the transport model for both catchments.

4.2.2. Stream discharges

A comparison between simulated and observed stream discharges showed major differences for the two catchments (Fig. 7). Differences were more marked for the Kerrien catchment, with a mean absolute difference of 0.79 mm d\(^{-1}\) between simulations and observations calculated over the whole period. This corresponds to 29% of the annual maximal variation of the stream discharge. In the Kerbernez catchment, the mean absolute difference was 0.23 mm d\(^{-1}\), corresponding to 25% of the annual maximal variation of the stream discharge. The differences between simulated and observed discharge remained constant over time.

4.3. Streamwater NO\(_3\) variations

4.3.1. Effect of NO\(_3\) concentration variations in recharge water

Stream nitrate concentration simulated with time-variable nitrate concentrations in the groundwater recharge did not exhibit a greater variability over time.
compared with the simulations using a constant concentration in the recharge. A comparison was carried out using these two types of nitrate recharge in the Kerbernez catchment, but it did not lead to any significant differences between the stream nitrate concentrations (Fig. 8). Therefore, to facilitate calculations for the subsequent simulations, nitrate concentrations in the recharge water were assumed to be constant over time, at 60 mg l\(^{-1}\).

### 4.3.2. Influence of spatial distribution of groundwater \(\text{NO}_3^-\) concentrations

For the Kerrien catchment, streamwater nitrate concentrations calculated with the NO3-KER data (spatial distribution of initial nitrate concentrations and a real extent of denitrification) lead to a seasonal pattern with maxima in March of each year. These late winter maxima are consistent with field observations (Fig. 9). Increasing the extension of the denitrifying zone from 2.5 to 5% of the catchment area has two major consequences. The first is to decrease the mean annual stream nitrate concentration from 44 to 34 mg l\(^{-1}\), hence increasing the mean absolute simulation error to 9 mg l\(^{-1}\). The second consequence is to increase the range of variation of the simulated nitrate concentrations. Indeed, differences between late winter (March) and late summer (September) were 25, 20 and 30 mg l\(^{-1}\), respectively, for the observations and for simulations with denitrification affecting 2.5 and 5% of the area. The simulated weekly nitrate fluxes were also systematically higher than the observed values (Fig. 10).

For the Kerbernez catchment, the NO3-KBZ spatial distribution gave acceptable results with a mean absolute simulation error of 2 mg l\(^{-1}\) using a denitrification extension of 0.5%. We also simulated a slight seasonal pattern with a winter minimum around February (Fig. 9). This pattern is consistent with the observations. However, the simulated concentrations in winter were higher than the observed ones. Despite a good agreement between the concentrations, the simulated nitrate fluxes in the stream were also nearly always overestimated for most of the time (Fig. 10). This underestimation could be related to the simulated stream discharges, which were systematically underestimated (Fig. 7). Moreover, the effect of denitrification was minor within the range of zone extension that we tested. This was probably due to the small spatial extension in the catchment (0.5% of the total catchment area). These simulations showed that a two-layer mixing model, with a vertical gradient of nitrate concentrations between the shallower layer (60 mg l\(^{-1}\)) and the deeper layer (80 mg l\(^{-1}\)), can explain a part of the streamwater nitrate variations. However, such a gradient model did not reproduce the whole variability observed in the streamwater, especially the lower concentrations during the autumn.

### 5. Discussion

One of the main results of the modelling is to show that variations of nitrate concentrations in streamwater do not reflect the nitrate concentration variations in soil water drainage, but derive from the spatial pattern of the groundwater chemistry. This is consistent with recent results showing that the seasonal variability of the solute concentrations in topsoil is progressively attenuated from the soil down to the water table by dispersion and diffusion mechanisms, as well as by the occurrence of denitrification in the soil but also in the WGL just above the water table (Legout et al., 2005). Moreover, this supports a previous hypothesis about hydrological and hydrochemical functioning (Molénat et al., 2002;
Fig. 9. Comparison between observed and simulated streamwater nitrate concentrations according to the NO3-KER (Kerrien catchment) and NO3-KBZ (Kerbernez catchment) distributions.

Fig. 10. Observed and simulated weekly nitrate fluxes (mg d\(^{-1}\)) in streams of the Kerbernez and Kerrien catchments. The dashed line represents the bisector.
Martin et al., 2004) in which the temporal patterns of stream nitrate concentrations with winter maxima can be explained by a uniform distribution of groundwater nitrate concentration coupled with denitrification in the stream riparian area. Conversely, seasonal patterns in stream nitrate concentrations with summer maxima can be explained by a two-layer mixing model, with higher nitrate concentrations in deeper parts of the WGL.

We develop two points in the discussion: (1) the relevance of the model with regard to stream discharge simulation and the contributions of the different domains to streamflow; (2) the groundwater response time following variations in the nitrate concentration of the recharge water.

5.1. Relevance of model

5.1.1. Stream discharges

Whatever the hydraulic conductivity values, the simulated stream discharges are overestimated with respect to the observed values in the Kerbernez and Kerrien catchments (Fig. 7). The modelling error is systematic, which implies that it does not arise from an incorrect temporal distribution of the simulated stream discharge. Ruiz et al. (2002b) faced a similar issue when modelling the hydrology of Kerrien and Kerbernez catchments, and had to consider in their modelling that only 60% of the water infiltrating in the soil was drained by the catchment reach. The error in the stream discharge simulation may be due to a sink that is not taken into account in the flow model. Two processes could explain the overestimation of the simulated stream discharges. The first hypothesis is that a fraction of the groundwater flux underflows the stream reach in each catchment, and discharges into the stream network downstream of the catchment outlet. The second hypothesis is that deep groundwater drainage occurs down to the bedrock fractures and faults. The latter hypothesis is consistent with geophysical surveys showing sub-vertical fractures at depths around 20–30 m (Fig. 1). The fractures provide preferential pathways for groundwater flow in weathered granite. Geophysical surveys show that fractures are quite deep in comparison to the stream reach elevation. Consequently, the groundwater flow in fractures is unlikely to exfiltrate within the catchment area, and should therefore occur downslope of the catchment outlet. This modelling illustrates clearly the difficulty of choosing the appropriate scale to study elementary processes in catchments. On the one hand, we tend to work on small catchments to focus on the process of interest. On the other hand, local heterogeneities such as fractures can have a profound effect on the hydrological or hydrochemical behaviour of small catchments.

5.1.2. Contribution of domains to streamflow

In the Kerrien catchment, the flow and transport models simulate stream nitrate concentrations as the result of a mixing between two domains: the highly concentrated upslope-midslope domain and the denitrified stream riparian zone. An analysis of the results shows that the relative contribution of the two domains in terms of water fluxes remains almost constant over the year, the upslope-midslope domain contributing approximately 70%. Consequently, the seasonal variations in stream nitrate concentrations simulated by the model do not result from variations in the water fluxes discharging from the two domains as proposed by Martin et al. (2004). The simulated variations arise mainly from variations in the nitrate concentrations in the water discharging from the riparian zone. In summer, nitrate concentrations in water flowing from the riparian zone are lower than in winter due to an increase in the denitrification fluxes. The denitrification in summer is more effective because the water residence time in the riparian zone is longer, allowing denitrification reactions to proceed even further. The increase in residence time in summer is a consequence of the water velocity decrease caused by a decrease of hydraulic gradients within the groundwater.

5.2. Groundwater response to variations of recharge concentration

From the modelling results, nitrate concentration distribution in groundwater would appear to be the key factor explaining the nitrate concentrations in stream water. The question is then why are the groundwater nitrate concentrations stratified in the upper slope domain of Kerbernez but almost uniform in the Kerrien catchment? We could assume that the distribution of groundwater nitrate is related to the
long-term variations of nitrate concentrations in soil water drainage, and hence linked to the history of the agricultural practices. To test this assumption, the flow and transport model was run for each catchment to investigate the groundwater response time to variations in nitrate concentrations in soil water drainage. We considered two types of evolution in catchment history: (i) an enrichment corresponding to much higher nitrate concentrations in water drainage than in the groundwater and (ii) a dilution corresponding to a decrease of concentrations in the water drainage. The enrichment evolution was represented according to a recharge with nitrate that remained constant over time (80 mg l$^{-1}$). This recharge was applied each day over 14 years in the groundwater, which was initially free of nitrate. The evolution of groundwater nitrate concentrations was followed in the upslope domain, at depths of 5 and 15 m.

At 5 m depth, groundwater nitrate concentrations increased rapidly and reached a plateau after approximately 14 years (Fig. 11A). At that time, the groundwater concentration reached 85–90% of the recharge concentration. Although seasonal cycles are clearly marked at the beginning of the period, they are progressively smoothed out when nitrate concentrations become close to the recharge concentration. We could account for the differences in seasonal dynamics at 5 m depth between the two catchments by the varying volume of the WGL, which is higher for Kerbernez than for Kerrien.

At 15 m depth, groundwater nitrate concentrations increased slowly, with an almost linear evolution, especially in the Kerbernez catchment. The increase of nitrate concentration begins earlier for Kerrien than for Kerbernez. After 14 years, the groundwater concentration reached 60–70% of the recharge.

![Fig. 11. Evolution of nitrate concentrations in groundwaters of the Kerrien and Kerbernez catchments, with an annual recharge concentration of 80 mg l$^{-1}$ nitrate, represented as a function of time (A) and depth (B). $C_0$ (80 mg l$^{-1}$) corresponds to the nitrate concentration in the water recharge. The 20 m depth corresponds to the WGL-bedrock interface.](image-url)
concentration. No clear seasonal variations of nitrate concentrations could be observed.

A comparison of nitrate enrichment at different times along a vertical profile in the groundwater (Fig. 11B) shows that, at the beginning of the simulation period, the rate of increase in nitrate concentration is higher in the shallower part of the WGL. By contrast, at the end of the simulation period, nitrate concentration increases more rapidly in the deeper part of the WGL. The transition between these two phases corresponds to a state of equilibrium between the shallower and the deeper parts of the WGL. This state was reached between 6 and 8 years for Kerrien, as against 10 and 12 years for Kerbernez. Moreover, at the end of the simulation period, differences between nitrate concentrations at depths of 5 and 15 m were higher for the Kerbernez than for the Kerrien catchment. This modelling suggests that equilibrium between concentrations in shallower and deeper parts of the WGL will be reached earlier in the Kerrien than in Kerbernez catchment. For both catchments, the time to reach equilibrium in the whole groundwater body following a variation in the recharge nitrate concentration is longer than 14 years. By taking similar WGL geometries and an initial state of nitrate concentrations, and applying the same recharge in both catchments, we arrive at two different simulated spatial distributions of groundwater nitrate concentration. The discrepancies arise from the differences in hydraulic head distribution within the aquifers of each catchment.

A dilution-type evolution was represented in the Kerbernez catchment by assuming a nitrate concentration decreasing from 80 mg l\(^{-1}\) down to 50 mg l\(^{-1}\) in the water recharge, with groundwater exhibiting a uniform initial nitrate concentration of 80 mg l\(^{-1}\). This evolution induces a strong decrease of groundwater nitrate concentrations in the shallower part of the WGL at 5 m depth within 5 years, and a linear decrease in the deeper part of the WGL (Fig. 12A). We also plotted the vertical distribution of nitrate concentrations at different times, along with the present vertical distribution observed in the Kerbernez catchment (Fig. 12B). This comparison supports the hypothesis that present-day Kerbernez groundwater nitrate concentrations have fallen from an initially high level and result from a decrease in the recharge concentration. According to our modelling, this decrease begun about 10 years ago.

The analysis of the groundwater response times leads to the conclusion that the dynamics of the Kerbernez catchment is clearly slower than the Kerrien catchment. These results are consistent with previous studies (Ruiz et al., 2002b; Martin et al., 2004), showing the important influence of spatial heterogeneities of physical and chemical properties on catchment behaviour.

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**Fig. 12.** Evolution of groundwater nitrate concentrations following a decrease of recharge concentration. \(C_0\) and \(C_f\) are the initial and final nitrate concentrations in the water recharge, respectively. The initial concentration in the groundwater is 80 mg l\(^{-1}\). The 20 m depth corresponds to the WGL-bedrock interface.
6. Conclusion

The main objective of this study is to improve our understanding of nitrate exportation by the stream in two neighbouring agricultural catchments by adopting a modelling approach. While building the model, water fluxes in catchments appeared to be less sensitive to WGL geometry than the spatial distribution of hydraulic conductivity. For both catchments, the best fit between observations and simulations was provided by a flow model with an upslope-downslope gradient of hydraulic conductivity. Seasonal patterns of nitrate concentrations in streamwater could be partly attributed to the spatial distribution of nitrate concentration in the groundwater. The lateral distribution of nitrate concentrations in groundwater derives from denitrification in the downslope domain. The vertical distribution in the Kebernez catchment appears to result from a decrease of the concentration in the water recharge. However, the range of seasonal variations of stream nitrate concentrations simulated by the model is underestimated, possibly due to an incorrect estimation of the contribution of the domains to streamflow.

This study also provides some information about reaction times of groundwater in response to variations in nitrate concentration in water recharge. The example of the Kerbernez catchment shows that decreasing nitrate concentrations in the recharge water to 50 mg l\(^{-1}\) (which corresponds to the maximum concentration level in drinking water specified by the European Community), can lead to consequences that are observed several years after the decrease in recharge concentration. For both catchments, following a variation in the recharge nitrate concentration, the time to reach equilibrium in the whole groundwater body is longer than 14 years. However, this response time corresponds only to transfer times in the groundwater. To evaluate the response time of the whole catchment, solute transport in the vadose zone and in the bedrock fractures need to be taken into account, as well as biotransformation kinetics due to nutrient cycles in soils. Finally, catchment response times would appear to be longer than groundwater response times. In a perspective of water quality restoration, we show that decreasing nitrate concentration in the recharge from 80 to 50 mg l\(^{-1}\) would result in a slow decrease of groundwater nitrate concentrations over 25 years. Based on these results, we argue for a more significant decrease of nitrate concentration in the recharge water (that is, in nitrogen supply by agriculture), in order to reach a groundwater concentration close to the maximum concentration level recommended by the European Community.

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References


