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Modelling flow and nitrate transport in groundwater for the prediction of water travel times and of consequences of land use evolution on water quality

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Abstract:

A two-dimensional model representing flow and nitrate transport in groundwater was developed and applied to a hillslope of the Kervidy catchment. The objective of the modelling was: (1) to characterize better the flow and nitrate transport in the groundwater and to determine the characteristic times of the system; (2) to explore the consequences of changes in nitrate leaching to groundwater on nitrate concentration in stream water. The finite-difference code MODFLOW was used to simulate the distribution of hydraulic head within the groundwater. Nitrate transport was described by the convection equation solved using MT3D. MODPATH was also used to analyse flow paths and travel times in the groundwater. Four units were considered in the model: (i) the plough layer, (ii) the soil, (iii) the weathered shale and (iv) the fissured shale. Autotrophic denitrification in the shale and partly in the weathered shale was represented, as well as heterotrophic denitrification in the upper horizon of bottom land. A steady-state average flow was assumed with a spatially uniform groundwater recharge of 2 mm day^{-1} , corresponding to the winter mean daily recharge observed in the Kervidy catchment. Nitrate recharge rate was fixed at 100 mg l^{-1} , which is equivalent to a nitrogen flux of $165 \text{ kg ha}^{-1} \text{ year}^{-1}$. Six scenarios of nitrate leaching changes were analysed with the model. The first two correspond to spatially uniform decreases of the nitrate recharge rate to 80 and 60 mg l^{-1} , respectively. In the other four scenarios, nitrate recharge rate was spatially distributed along the hillslope so that the average nitrogen flux remained equal to $165 \text{ kg ha}^{-1} \text{ year}^{-1}$. Simulated hydraulic heads were similar to observed values along the hillslope, except for the summit. The transport model reproduced the spatial pattern of nitrate concentrations observed in the weathered shale groundwater, a deviation appearing only in the nearest piezometer to the stream. Travel times within the groundwater appeared to be highly variable, from a few days up to 3 years. Scenario analysis showed that a significant decrease of stream nitrate concentration can be expected following a global decrease in nitrate leaching along the hillslope. However, the fall could be very gradual in time.

KEY WORDS groundwater flow; nitrate transport; denitrification; travel time to stream; flowpath; land use evolution; French Brittany

INTRODUCTION

Over the three last decades, French Brittany has become one of the most productive agricultural regions in Europe. The agriculture has consisted mainly of animal production, like pig and poultry farming. The intensification of agriculture has been accompanied by an increase of nitrate concentrations in surface water. Some 80% of this water currently exceeds the European Community threshold of nitrate concentrations in drinking water ($11.3 \text{ mgN-NO}_3^- \text{ l}^{-1}$) in Brittany, where surface water provides most of water consumed (Institut Français de l'Environnement, 1997). Together with the sanitary consequences, high nitrate concentrations in surface water cause ecological damage to aquatic life through algae blooms and eutrophication.

Traditional land use and manure applications need to be better managed to stop or at least to reduce water pollution. Therefore, different strategies for land use and agricultural management have been suggested to

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reduce nutrient loads in surface water. One strategy consists of accounting for the spatial distribution of crops, and more generally the spatial organization of agricultural practices in the catchment. In other words, the effect of a given crop on nutrient export to a stream would depend on its location in a catchment. The efficiency and impact of these strategies need to be evaluated by considering the extent of the decrease in nitrate concentration and the length of time required to restore water quality. In this context, there is a clear need for knowledge and tools to assess the efficiency and consequences of strategies used to reduce water pollution. Modelling appears to be one of the approaches to investigate the impacts of land-use changes and alternative agricultural practices on water quality at the catchment scale.

Our first objective was to understand and describe the fate at the catchment scale. Since shallow groundwater controls hydrology in the region, the study focused on spatial and temporal distribution of nitrate in groundwater of a well-studied catchment. From all the information collected in the catchment, we constructed a model of flow and nitrate transport in groundwater. The modelling was carried out to characterize the flow and nitrate transport in the groundwater system and to provide a first estimation of water residence time in the groundwater. Furthermore, as a first approach to evaluate the impact of agricultural practices evolution, six scenarios were established, each one corresponding to a different nitrate leaching. The consequences of each scenario on nitrate concentration in stream water were investigated.

BACKGROUND

Site description and equipment

The study was carried out in the Kervidy Catchment (KC), a 5 km² sub-basin of the Naizin catchment (12 km²), located in central Brittany, France (Figure 1b). This site has been the subject of many studies for its agriculture, soils, geology and hydrology (Curmi *et al.*, 1996; Durand and Juan-Torres, 1996; Cheverry, 1998). The catchment is underlain by fissured and fractured shale, the upper part of which is weathered (Figure 2b). Slopes are generally moderate, not exceeding 10%, and the elevation ranges from 98 to 140 m above the sea level. The climate in the area is humid and temperate. The annual mean rainfall and annual potential evapotranspiration (PET) are 909 mm (period 1968–1997) and 690 mm (period 1996–1999) respectively.

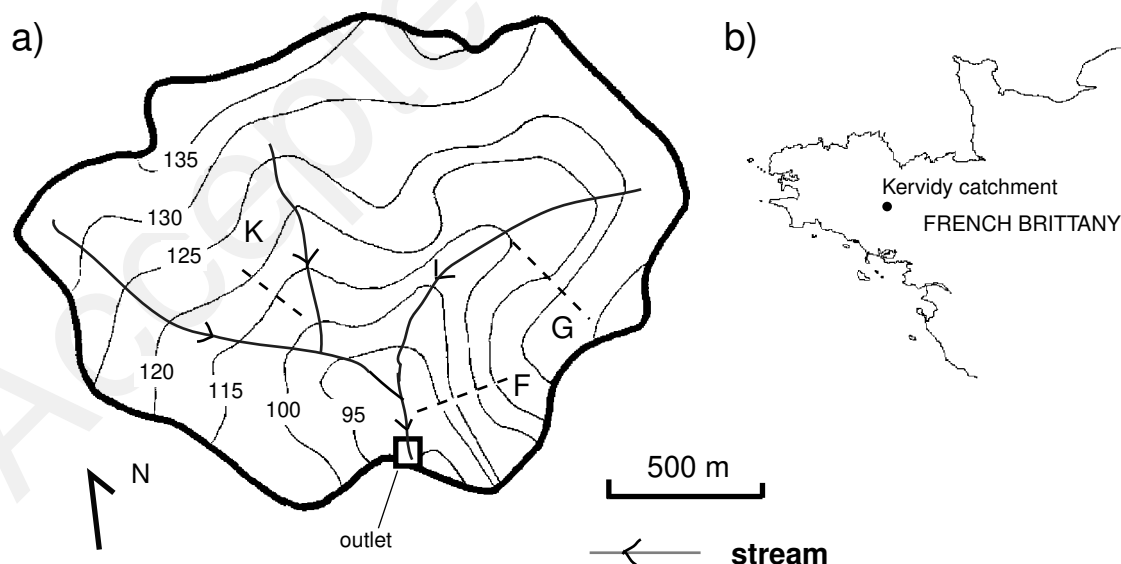


Figure 1. Location of the KC (b) and observation hillslopes [dashed lines in (a)]

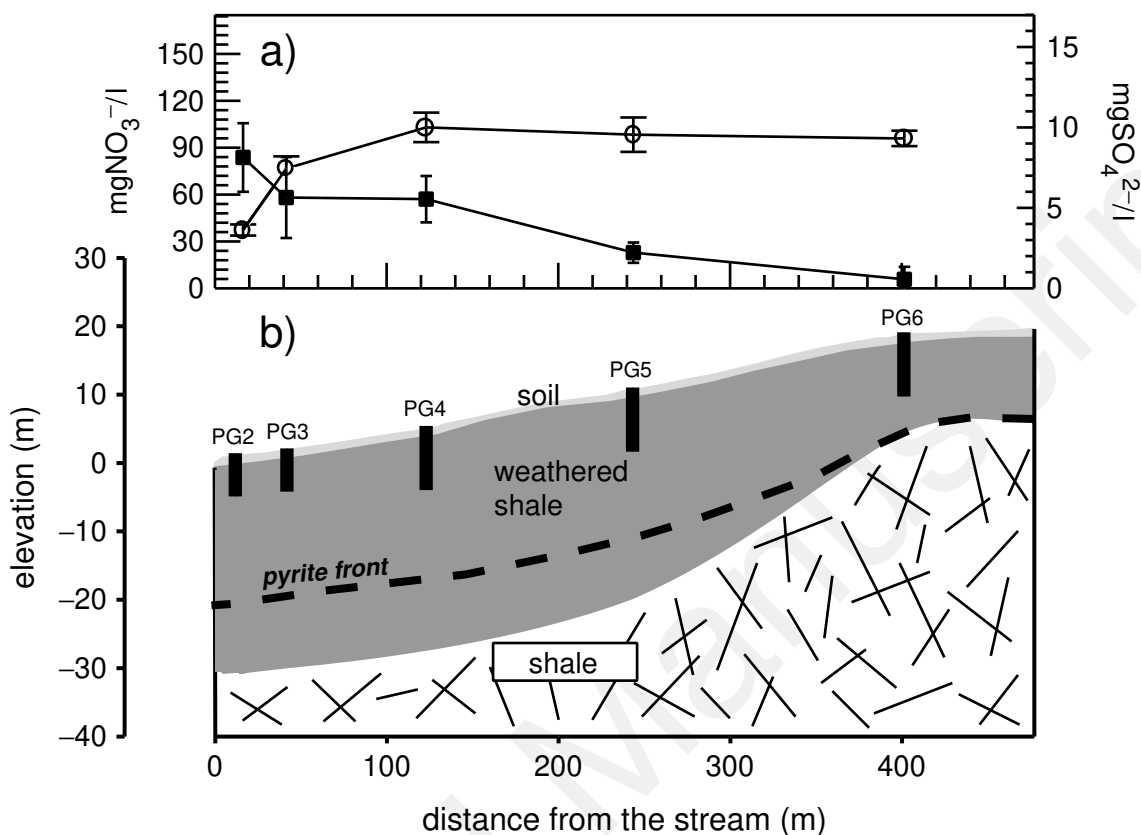


Figure 2. Cross-section of the hillslope G showing the three main formations: the soil, the weathered shale and the shale (b). Nitrate (white circles) and sulfate (black squares) concentrations observed in piezometers along the hillslope are also displayed (a)

Over the last 5 years, stream runoff ranged from 200 to 500 mm. The groundwater, which develops in the soil, the weathered shale and the shale, is shallow. Water table depth ranges from a few centimetres in bottom lands to less than 10 m in summits. The groundwater plays a dominant role in the hydrology of the KC, contributing 97% of stream discharge (Molénat *et al.*, 1999).

Some 90% of land surface is used for agriculture. Agriculture is intensive leading to an average annual nitrogen excess throughout the last decade of about 190 kg ha^{-1} (Bouraoui *et al.*, 1999).

Stream runoff at the outlet of the KC has been recorded every 10 min since 1993. A weather station located within the Naizin catchment provided hourly rainfall and daily Penman PET. To study the spatial and temporal distribution of nitrate concentration in the groundwater, 15 piezometers were installed along three hillslopes, named F, G and K (Figure 1a). All of these piezometers were designed to intercept the groundwater in the weathered shale (Figure 2b). The piezometer depths varied from 3 to 10 m, depending on the location (Table I). They consisted of 11 diameter cm PVC tubes slotted at the base. Deep piezometers reaching the shale groundwater were also installed in the Naizin catchment. A 40 m deep piezometer was located very close to the outlet of the KC.

Soils of the KC developed on a silty material that is a mixture of weathering products and Quaternary eolian deposits. Soil thickness varies from 0.5 to 2 m. Prior to our study, a detailed hydrodynamic characterization of the soils was also realized from undisturbed soil blocks, providing saturated hydraulic conductivity and a water retention curve (Curmi *et al.*, 1996). The upper part of the shale is weathered to a highly variable thickness, ranging from 1 to 30 m depending on the location. Hydrodynamic characterization of the weathered

Table I. Piezometers characteristics of hillslopes K, G and F in the KC. The reference for elevations is the stream bottom

	Piezometers of hillslope G					Piezometers of hillslope K				Piezometers of hillslope F			
	PG2	PG3	PG4	PG5	PG6	PK1	PK2	PK3	PK4	PF4	PF1	PF3	PF4
Distance (m)	16	42	123	244	401	36	98	187	222	4	84	174	281
Elevation (m)	1.1	1.8	4.8	10.6	18.8	1.23	3.00	5.24	6.99	0.7	6.7	15.4	22.1
Slotted depths (m)	2–3	4–8	4–8	4–8	4–8	2–3	2–3	3–4	3–4	1.5–2	4–5	4–5	7–10

shale was carried out by performing slug tests in three piezometers of hillslope G and in three piezometers of hillslope K. Slug tests provide an estimate of hydraulic conductivity around the immediate vicinity of the piezometers. Hydraulic conductivity was found to be variable within one order of magnitude, ranging from 4×10^{-6} to 2×10^{-5} m s⁻¹. Pumping tests were also carried out in deep piezometers. Although the shale was fissured and fractured, as a first approximation the tests showed that this formation could be regarded as an homogeneous porous aquifer (Martelat and Lachassagne, 1995; Pauwels *et al.*, 1996). From these tests, the total porosity and the hydraulic conductivity of the shale were estimated at 1×10^{-3} m³ m⁻³ and 3.5×10^{-7} m s⁻¹ respectively.

Groundwater samples in hillslope K and stream samples were collected fortnightly over 2 years, from January 1997 to December 1999. Groundwater in hillslopes G and F was sampled for 1 year (December 1998–December 1999). One sample was collected in February 1998 in the 40 m deep piezometer. Physico-chemical parameters, such as pH and redox potential, were measured in the field. Samples were filtered (0.2 µm) and analysed in the laboratory for nitrate, sulfate and chloride concentrations by ion exchange chromatography. Field equipment and sampling methods are documented extensively in Molénat *et al.* (in press).

Nitrate distribution in groundwater

The groundwater displayed small temporal variations of nitrate and sulfate concentrations. The nitrate and sulfate concentrations in the weathered shale groundwater exhibited similar spatial patterns along the three hillslopes. Nitrate concentrations and sulfate concentrations displayed uphill and downhill gradients respectively (Figure 2a). Nitrate concentrations decreased downhill from 100 to 40 mg l⁻¹, from 180 to 4 mg l⁻¹ and from 130 to 80 mg l⁻¹ for hillslopes G, F and K respectively. Sulfate concentrations were low in all the piezometers located in the summits of the hillslopes (<1 mg l⁻¹) and ranged from 10 to 28 mg l⁻¹ in the piezometers located at the bottoms of the hillslopes (Figure 2a). Chloride concentrations ranged from 25 to 50 mg l⁻¹. The pH also displayed a continuous downhill gradient from pH 5 to nearly pH 7. In contrast, the redox potential was constant along each hillslope at around 400 mV. In the shale, nitrate, sulfate and chloride concentrations were of 2.8 mg l⁻¹, 20.8 mg l⁻¹ and 18.0 mg l⁻¹ respectively.

The weathered shale groundwater in the KC appeared to be the major hydrologic storage of nitrate controlling the export of nitrate to the stream. To explain the strong spatial pattern in the weathered shale groundwater chemistry, the most likely hypothesis is a dilution with water containing a low level of nitrate (Molénat *et al.*, in press). Following this hypothesis, the shale groundwater is a consistent end member, as the water was poor in nitrate and rich in sulfate. Low nitrate concentrations would result from autotrophic denitrification together with the oxidation of pyrite (FeS₂), which is present in the shale, and the consequent production of sulfate (Pauwels *et al.*, 1998). Upward flows of deep denitrified groundwater to the weathered shale aquifer explain both the nitrate and sulfate distributions we observed in the upper layer of the weathered shale groundwater. Soil water in the upper horizons of bottom lands would also be an appropriate end member, since it was shown that heterotrophic denitrification took place in these horizons, resulting in low nitrate concentrations in this water (Durand *et al.*, 1998). However, water from these horizons is most likely to flow directly to the stream rather than down to the weathered shale groundwater.

Denitrification in the upper part of weathered shale groundwater along flowpaths or a spatial pattern in nitrate leaching from soil surface could not be invoked to explain the spatial pattern in the weathered shale groundwater chemistry (Molénat *et al.*, in press). The denitrification would imply a decrease of redox potential and the presence of electron donors. Neither were observed in the field. In particular, the dissolved organic carbon concentration in the weathered shale groundwater, as well as in the shale groundwater, was low, and did not exceed 3 mg l^{-1} . A spatial pattern in nitrate leaching would imply a systematic spatial organization of cultural and fertilization practices, which has not been identified in the KC.

MODELLING

Groundwater modelling

So far, we have speculated that the spatial distribution of nitrate concentration in the weathered shale groundwater comes from upward flows from denitrified deep water. The objectives of the modelling were twofold: first, to characterize better the flow and nitrate transport in the groundwater system of the KC and to determine the characteristic times of the system; second, to explore the consequences of changes in nitrate leaching to groundwater on stream water nitrate concentrations.

To achieve these objectives, we developed a two-dimensional model representing flow and nitrate transport in a vertical section perpendicular to the groundwater surface. The section we selected corresponded to hillslope G (Figure 2b). The finite-difference code MODFLOW was used to simulate the distribution of hydraulic head within the groundwater (McDonald and Harbaugh, 1988). Nitrate transport was described by the convection–dispersion equation solved using MT3D (Zheng, 1990). MODPATH was also used to analyse flow paths and travel times within the groundwater (Pollock, 1994).

The basic idea of our modelling was to build a rather simple model that could reproduce the distribution of the two main variables of the groundwater, i.e. the nitrate concentration and hydraulic head, and hence the main characteristics of the system. In the model, the simplifications were based on three hypothesis: (i) each formation was homogeneous and isotropic, (ii) the system was in a steady state average flow condition and (iii) the recharge was uniform along the hillslope. Local temporal or spatial variability could exist in the system, but we considered that this variability was of second order in the definition of the system. Hydraulic conductivity in the weathered shale aquifer appeared from the field estimations to be variable, but only within one order of magnitude. In this case, we considered that flow and nitrate transport was defined more by the variability from one formation to another than by variability within a given formation. Recharge could also vary in time, and hence induce a transitory state in the groundwater; however, we assumed that flowpaths within the system would not change. The hillslope was divided vertically into four units: (i) the plough layer at the soil top, (ii) the soil, (iii) the weathered shale and (iv) the fissured and fractured shale. The soil surface obtained by topographic survey was used as the top limit of the plough layer. The thickness and depth of each layer were variable in space and fixed on the basis of geological and pedological surveys (Figure 2b). The plough layer and the soil thickness were assumed to be uniform at 0.4 m and 1.5 m respectively. Hence, the slope of these layers corresponded to soil surface slope. The thickness of the weathered shale decreased downhill, from 13 to 30 m. The base of the shale aquifer was fixed at a depth of 70 m. Formations were subdivided into finer layers to respect numerical stability criteria for the resolution of the transport equation. The grid sizes were variable, depending on location, but never exceeded 5 m, both vertically and horizontally.

The hydraulic conductivity for each unit was calibrated by trial and error (Table II). The calibration consisted in fitting simulated hydraulic heads to the observed heads while keeping the hydraulic conductivity values in the initial estimated known range.

Water velocity was estimated knowing the spatial distribution of hydraulic head and the hydraulic conductivity and effective porosity of each formation (Table II). For the fissured and fractured shale, the effective porosity was taken as equal to the total porosity. For the loamy silt and clay mediums, which are the weathered shale, the soil and the plough layer, the effective porosity was considered as equal to the specific

Table II. Parameters for the groundwater flow and nitrate transport model of hillslope G

	Hydraulic conductivity (m s^{-1})	Effective porosity ($\text{m}^3 \text{ m}^{-3}$)
Plough layer	1×10^{-4}	0.2
Soil	5×10^{-5}	0.2
Weathered shale	8×10^{-6}	0.05
Shale	8×10^{-7}	0.002

yield. Since convection was assumed to be the main process in nitrate transport, dispersion and molecular diffusion were neglected in the model.

Groundwater boundaries

The model was run assuming a steady state average flow condition corresponding to winter. To fix the groundwater recharge rate we assumed that effective rainfall was a good estimate of the recharge. Analysis of water table variations showed that groundwater recharge occurred in winter in response to each rainfall event (Molénat, 1999). Considering the effective rainfall as the difference between direct rainfall and PET, level variations appeared to be roughly equal to the effective rainfall during the event divided by the drainage porosity. Furthermore, analysing the rainfall over the last 6 years revealed that, apart from the winters of 1994–1995 and 1996–1997, the winter mean daily effective rainfall varied within a narrow range at around 2 mm day^{-1} (Table III). The winters of 1994–1995 and 1996–1997 were very wet and very dry respectively, and thus did not appear to be representative of average winter condition (Table III). Therefore, groundwater recharge was fixed at 2 mm day^{-1} . Evapotranspiration was then implicitly accounted for by assuming the effective rainfall as the groundwater recharge.

We assumed no lateral flow at the top of the hillslope and at the base of the shale, a constant head in the stream water and a uniform recharge along the hillslope.

Nitrate concentration in the recharge was fixed at 100 mg l^{-1} , which corresponded to the nitrate concentration in piezometers PG5 and PG6 (Figure 2a). The nitrate concentrations in PG5 and PG6 were considered to be representative of the nitrate concentration in recharge for two reasons: first, because these piezometers intercepted the groundwater around the water table; second, because the piezometers were located in the summit of the hillslope (Figure 2b). So, nitrate concentration at these points was controlled mainly by recharge concentration, and upslope area contribution to these points could be assumed to be insignificant. The recharge was considered uniform over the hillslope, any spatial distribution of nitrate leaching was assumed to be of second order.

From an initial uniform nitrate concentration of 20 mg l^{-1} in the whole groundwater, the spatial and temporal distributions of groundwater nitrate concentrations were computed until equilibrium was reached.

Denitrification processes

Autotrophic and heterotrophic denitrifications were described in the model by a first-order reaction. In the KC, heterotrophic denitrification occurs in hydromorphic soils, which correspond to a 40 cm thick layer from

Table III. Mean daily effective rainfall and total rainfall in winter for the last 6 years in the KC

	1994–95	1995–96	1996–97	1997–98	1998–99	1999–2000
Daily effective rainfall (mm day^{-1})	4.90	2.15	1.16	2.19	2.15	2.05
Total winter rainfall (mm)	480	246	115	217	207	203

the soil surface extending to over 60 m from the stream. Previous studies on heterotrophic denitrification in hydromorphic soils of the KC revealed that rates were very high, such that nitrate was completely reduced within a few hours, especially when initial concentrations were high (Durand *et al.*, 1998). The kinetics of heterotrophic denitrification were not estimated. However, a first-order reaction with a very small half-life seemed to be appropriate to describe the fast nitrate reduction observed in the field. Thus, the half-life of heterotrophic denitrification was fixed at 0.5 day. Autotrophic denitrification was assumed to occur in pyrite-rich layers. Deep drillings revealed that, in hillslope G, pyrite was present in all the shale and in the weathered shale beyond 20 m deep (Figure 2b). The half-life was fixed at 5 days, in accordance with field tracer tests performed in the shale aquifer of Naizin by Pauwels *et al.* (1998) showing that autotrophic denitrification could be described by a first-order equation with a half-life ranging from 2.1 to 7.9 days. As outlined by Pauwels *et al.* (1998), these rates were amongst the highest recorded in the literature for this reaction and confirmed the need for denitrification rates to be evaluated for a specific aquifer rather than to be extrapolated from one aquifer to another one.

Scenarios

Six scenarios were studied. These scenarios were assumed to represent the evolution of Brittany's agriculture towards better management practices. In regions of intensive agriculture, many alternative solutions to the current situation have been proposed in order to restore water quality. One of them would be to reduce nitrate leaching from all fields. This solution was employed in the first two scenarios, where a uniform decrease of nitrate concentration was applied to the current recharge. So, nitrate concentration in the recharge was reduced to 80 mg l⁻¹ in scenario 1 and to 60 mg l⁻¹ in scenario 2. Other solutions for the restoration of water quality are based on the idea that, for a given average nitrate leaching rate at the catchment scale, an optimum spatial distribution of nitrate leaching rate would allow a minimum nitrate concentration in stream water. In other words, there would be an optimum spatial organization of agricultural land use leading to a minimum impact on water quality. This solution was used in the final four scenarios, where nitrate concentration in recharge was spatially distributed (Figure 3). In scenarios 3 and 4, the hillslope was divided into two zones of equal length. In scenario 3, nitrate concentrations were fixed at 50 mg l⁻¹ in the most downslope half of the hillslope (zone A) and at 150 mg l⁻¹ in the most upslope half (zone B). In scenario 4 we inverted the distribution, such that the nitrate concentrations were 150 mg l⁻¹ downslope and 50 mg l⁻¹ upslope. In scenarios 5 and 6,

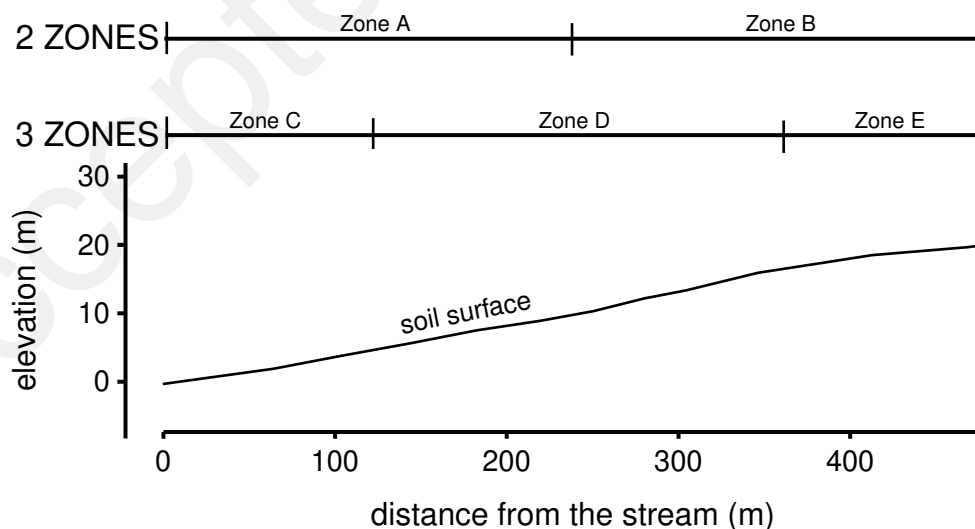


Figure 3. Hillslope discretization for the scenario study. Zones A and B are of the same length. Zones C and E are half the length of zone D

three zones were considered, such that the top zone (E) and the bottom zone (C) were both half the length of the middle zone (D). In scenario 5, the nitrate concentrations for zones C, D and E were fixed at 50 mg l^{-1} , 150 mg l^{-1} and 50 mg l^{-1} respectively. In scenario 6, the nitrate concentrations were 150 mg l^{-1} for zones C and E and 50 mg l^{-1} for zone D.

The average nitrate fluxes to the groundwater were $132 \text{ kgN ha}^{-1} \text{ year}^{-1}$ and $99 \text{ kgN ha}^{-1} \text{ year}^{-1}$ for scenarios 1 and 2 respectively. The final four scenarios, based on a spatially distributed concentration, corresponded to a spatially average flux to the groundwater similar to the current one, i.e. $165 \text{ kgN ha}^{-1} \text{ year}^{-1}$. Each scenario was applied from an initial groundwater state corresponding to the equilibrium reached with the current nitrate concentration in recharge.

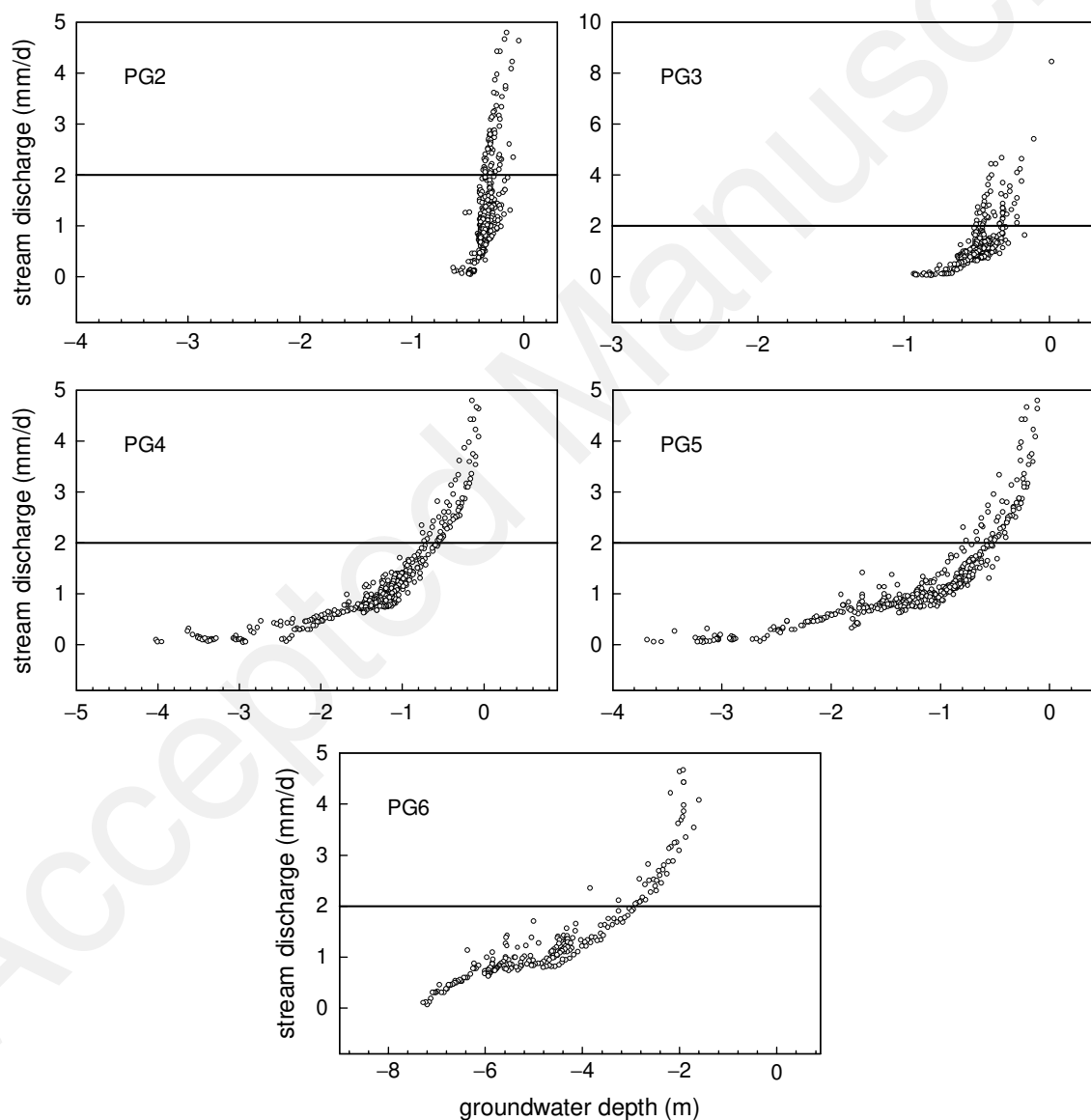


Figure 4. Relationship between the stream discharge and the groundwater depth in the piezometers of hillslope G, at KC

RESULTS

Hydraulic head and nitrate concentration simulations

Model results were compared with hydraulic heads in the weathered shale aquifer where observations were available. Since an almost one-to-one relationship between stream discharge and water table depth can be established for each piezometer (Figure 4), the hydraulic heads corresponding to a discharge of 2 mm day^{-1} were taken for comparison. Globally, the model reproduces the observed hydraulic heads well (Figure 5). The mean error (ME) and the mean absolute error (MAE) are 0.8 m and 1.10 m respectively. However, the difference between observed and simulated hydraulic heads increased uphill. Indeed, differences were small in the bottom and midslope points, ranging from 0.1 to 0.5 m (PG2 to PG4). The differences were larger for PG5 and PG6, at 1.6 m and 2.9 m respectively.

Simulated nitrate concentrations were also compared with the observed values (Figure 5). As anion concentrations were nearly constant in time, we took the annual average concentrations over 1997–1998 as the observed values. The nitrate concentration ME and MAE were estimated at 3.8 mg l^{-1} and 7.9 mg l^{-1} respectively. The decrease of nitrate concentration along the hillslope was represented by the model, but the nitrate concentration simulated in the nearest piezometer to the stream (PG2) was higher than the average annual concentration. The nitrate concentration deviation at this point was 24 mg l^{-1} , corresponding to an error of 61%. For all the other piezometers, the nitrate concentration deviations between observation and simulation did not exceed 6 mg l^{-1} , corresponding to a maximum error of 5%. Although the observation of nitrate concentration in the stream at the outlet of the KC was also available, comparing this observation with the model simulation would not have been meaningful. Stream water at the outlet integrates the discharge of all the hillslopes of the catchment, and field studies showed a great variability of nitrate concentrations in groundwater from one hillslope to another one.

Flowpaths and travel times

Path lines and travel times analysed using MODPATH showed three main flow paths in the groundwater along the hillslope (Figure 6b). The longest one corresponds to downward flows from the weathered aquifer to the shale aquifer in the uppermost part of the hillslope. In the lower part of the hillslope, this path comes upward from the shale aquifer to the stream through the shale weathered aquifer and the soil. The second path

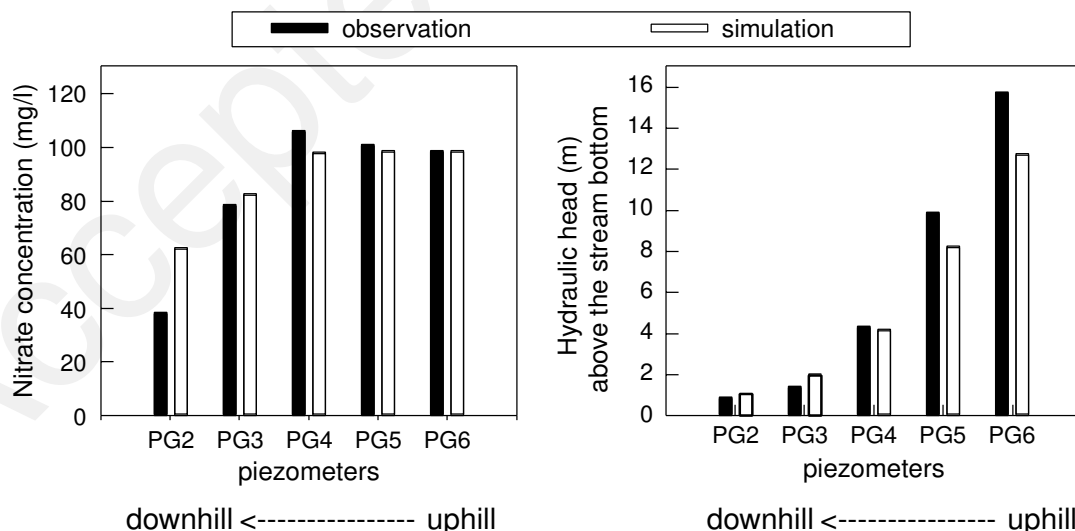


Figure 5. Observed and simulated nitrate concentrations (left) and hydraulic heads (right) along the weathered shale groundwater of hillslope G, at KC

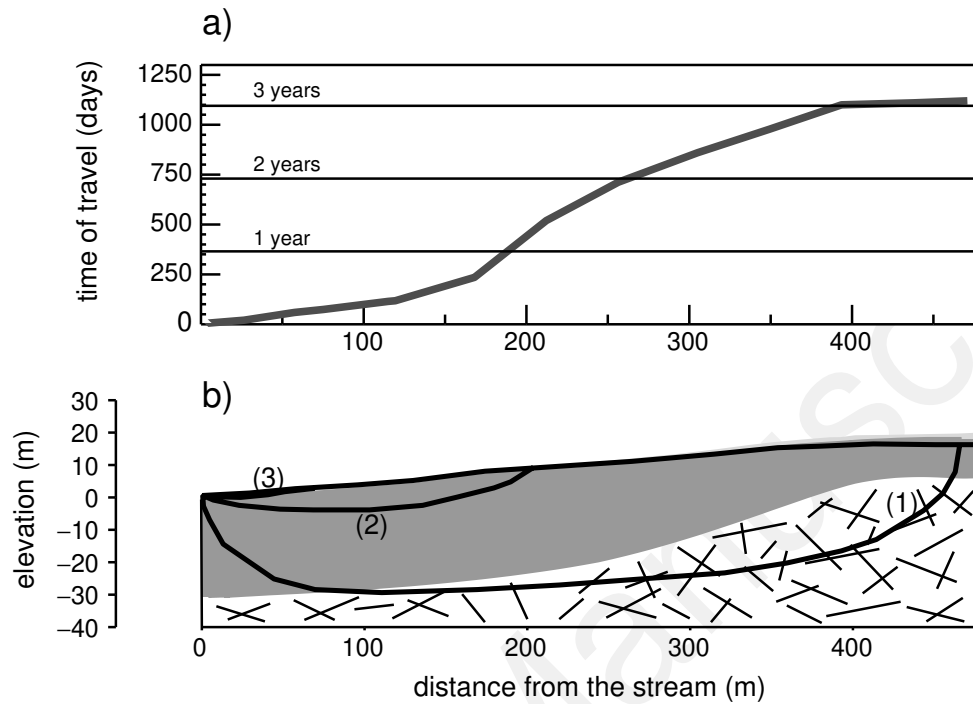


Figure 6. The three main flow paths (b) and residence times (a) of water computed by numerical modelling (MODFLOW, MODPATH) along hillslope G, at KC

flows from the midslope through the weathered aquifer and the soil to the stream. The third path corresponds to water flowing only through the soil plough layer and the soil straight to the stream. Figure 6a also presents the travel time of a virtual non-reactive particle depending on where the particle entered the groundwater. The travel time appeared to be highly variable, ranging from a few days for a particle entering in the bottom land up to 3 years for a particle entering in the summit. From the model, any particle entering in the uppermost 60% part of the hillslope would have a residence time in the groundwater of more than 1 year.

Scenarios

The nitrate concentration in the stream at equilibrium and the time to reach this equilibrium were analysed for each of the six scenarios. The current nitrate concentration in the recharge results in a simulated

Table IV. Simulated nitrate concentration in the stream water for each scenario and difference compared with the current situation

Scenario	Nitrate concentrations (mg l^{-1})	Difference (%)
Current situation	57.4	—
1	45.9	-20.0
2	34.4	-40.0
3	52.4	-8.9
4	62.0	+7.9
5	67.8	+17.9
6	46.3	-19.5

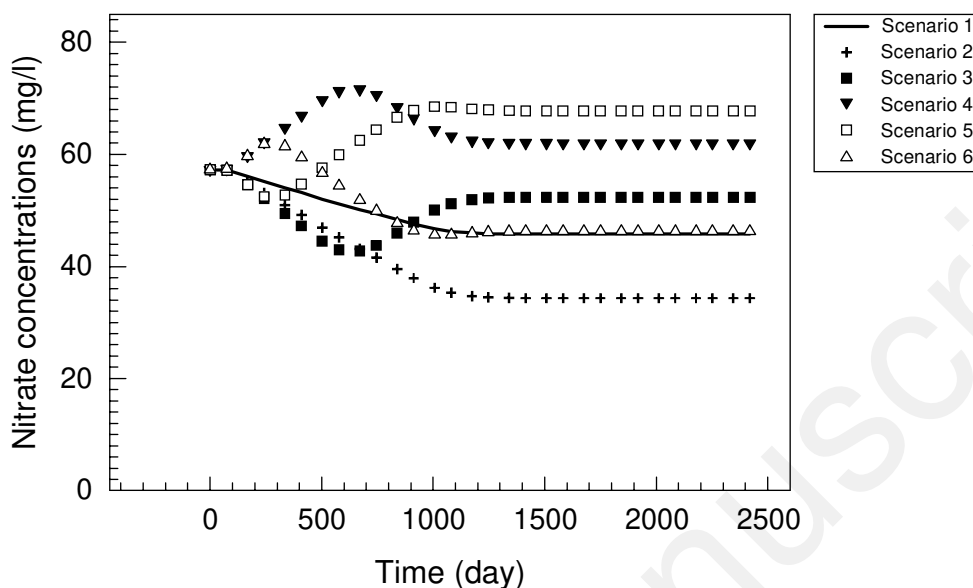


Figure 7. Simulated evolution of the nitrate concentration in the stream for each of the six scenarios

nitrate concentration in the stream of 57.4 mg l^{-1} (Table IV). The greatest changes of stream water nitrate concentration were obtained following a global and uniform reduction of nitrate leaching (scenarios 1 and 2). When nitrate leaching to the groundwater was distributed upon two zones (scenarios 3 and 4), changes in nitrate concentration were rather small and not greater than 9%. Changes from the current situation appeared to be more pronounced when distribution of nitrate leaching was made upon three zones. Higher nitrate concentrations in the midslope would cause an increase of nitrate concentrations in the stream (scenario 5), whereas higher nitrate concentrations in the upper zone and in the bottom land would cause a decrease of nearly 20% (scenario 6). The time and the concentration evolution to reach the equilibrium reflected the variability of travel time within the groundwater (Figure 7). Equilibrium is reached after about 1200 days. Three patterns can be observed in the evolution of nitrate concentration. The first pattern corresponds to a progressive decrease starting in the first 100 days (scenarios 1 and 2). The second pattern is characterized first by an increase and then a decrease (scenarios 4 and 6), and the third pattern presents a decrease followed by an increase (scenarios 3 and 5).

DISCUSSION

Groundwater flow and denitrification processes

The model was based on simplifications, some of which may explain the discrepancy between simulated and observed hydraulic heads in the summit of the hillslope. However, from the flow model simulations, the nitrate transport model reproduced the decrease of nitrate concentration in the weathered shale aquifer along the hillslope. From simulations, the decrease results from upward flows from deep denitrified groundwater, as we had hypothesized from the field observation analysis. Yet simulated nitrate concentration in piezometer PG2 was greater than that observed. The difference may be due to denitrification within the upper part of weathered shale, which was not represented in the model. However, if denitrification had occurred in all the weathered shale aquifer we would have observed a progressive downhill decrease of nitrate concentration from PG6 to PG2. Instead, the decrease is restricted to piezometers PG2 and PG3. The deviation between simulation and observation at piezometer PG2 raises the question of the difference between the scale of

measurement and the scale of modelling (Blöschl and Sivapalan, 1995). It is indeed difficult to compare measured concentration, which is a point value, with simulated concentration, which is representative of a cell with a size of a few metres. In particular, around the stream the flowpaths converge, resulting in high spatial variability of groundwater nitrate concentration. As suggested by Blöschl and Sivapalan (1995), rather than comparing the point values with grid values, spatial patterns of state variables could be used to assess the accuracy of models. In this way, our model reproduces the main characteristic of the groundwater chemistry, which is the strong spatial pattern of nitrate concentration. Differences obtained for the piezometer PG2 can be attributed to local heterogeneity in medium properties, which are not taken into consideration in the model. Eventually, the model can be considered as a good first-order quantification of the flow and the nitrate transport in the groundwater of hillslope G. The simulated nitrate concentration in the stream is 57.4 mg l^{-1} . Thus, with 100 mg l^{-1} in recharge, some 42.6 mg l^{-1} present in the groundwater recharge is denitrified within the groundwater. From simulations, it appears that one half of the nitrate removal is caused by autotrophic denitrification in the pyrite-rich layers, the remainder being attributed to heterotrophic denitrification. So far, denitrification and flow in bottom lands has been the focus of much of the interest, as they are thought to play a major role in stream water chemistry. This is confirmed by these results. Though the model calibrations and results are necessarily dependant on the assumed boundary conditions, the results do also suggest that flows from the deepest layers of the weathered shale and from the shale also affect stream water chemistry.

Travel times and land use evolution consequences

The time scale of nitrate transport in the groundwater of the KC, as simulated by the model, cannot be characterized by a single residence time. Instead, the time scale ranges from a few days to many years (Figure 6a), with important implications for water quality restoration. In terms of land use and agricultural management practices, any reduction in the nitrate leaching to groundwater will cause an immediate but gradual decrease in stream nitrate concentration. So, in catchments where stream water is highly contaminated by nitrate, persistent high nitrate concentration can be expected even if remediation measures are undertaken. In this work, the longest travel time was estimated to be more than 3 years. Yet the model did not take into account the immobile water corresponding to water in micro-porosity or in dead-end pores, as is the case for shale and weathered shale. In shale this corresponds to open fractures and small fissures (Pauwels *et al.*, 1998). Although the micro-morphology of weathered shale has not been studied in detail, visual observations when trenches were dug allowed the distinction between large pores where water flows out and a second type of much finer porosity where water flows much more slowly. Nitrate transport may be slowed down by molecular diffusion between mobile water and immobile water. Moreover, simulations were realized under winter recharge conditions, which correspond to the highest hydraulic gradients in the year and so to the fastest water velocity. Consequently, the simulated groundwater travel times obtained from the modelling must be regarded as an underestimate of the real ones. Furthermore, we do not consider here nitrate travel time from soil surface to water table. Since water velocity in the unsaturated soils of Brittany has been estimated at around 2 m year^{-1} (Gascuel-Oudoux and Mérot, 1986), nitrate travel time to reach groundwater can exceed 1 year in the area located in the summit of the hillslope, where water the table is more than 2 m deep.

This work agrees with other recent field studies showing that, even for shallow groundwater, water residence times may vary a lot depending on flow paths and may exceed many years and even many decades (Böhlke and Denver, 1995; Tesoriero *et al.*, 2000). This contradicts approaches such as the export coefficient method (Johnes, 1996). Such approaches assume that the time scale of nitrate export from soils to stream is short enough to be neglected.

Managing land use has often been put forward as a way to limit and even to reduce nitrate contamination in stream water. Results of the simulated scenarios show that, for the same spatially average nitrate leaching at the hillslope scale, variations of nitrate concentration in the stream can be expected depending on the spatial distribution of leaching (Table IV). As an example, scenarios 1 and 6 lead to almost the same nitrate concentration, whereas average nitrate leaching was $132 \text{ kgN ha}^{-1} \text{ year}^{-1}$ for scenario 1 and of

165 kgN ha⁻¹ year⁻¹ for scenario 6. Scenario 6 takes efficient advantage of denitrification processes. In this scenario, the highest nitrate recharge rates are added to the most upslope and downslope zones, which are the starting points of flows travelling through denitrifying layers (Figure 6b). However, a radical decrease of nitrate concentration in stream water would require a global and large reduction of average nitrate leaching, as suggested by the result of scenario 2.

CONCLUSION

The basic idea underlying this work was to build a simple model to characterize the groundwater flow in the KC, to analyse the controls of nitrate concentration distribution in the groundwater and to estimate the water travel times. The results confirmed the role of denitrified deep groundwater on nitrate decrease along the hillslope and showed a great variability of travel times. It is recognized that the results depend on the assumed boundary conditions, but, as a first approach, the modelling allowed us to investigate the consequences of six scenarios of nitrate leaching on stream water chemistry. The next step of this modelling would encompass the following steps. First, we would need to consider a dynamic state with a variable groundwater recharge in time. Second, the travel times computed by the model would have to be validated further. The assessment of the model on hydraulic heads and nitrate concentrations must be considered as the first step. Direct estimation of travel times from water age dating methods based on tracers could be a way to go further in the validation. For that, this first modelling provides a useful framework of flow paths and a first rough estimation of the time scale of water transfer. Therefore, as groundwater could be up to a few years old, we would need to use tracer methods allowing water age to be estimated with a temporal resolution not exceeding 1 or 2 years.

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