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Solute transfer in the unsaturated zone-groundwater continuum of a headwater catchment

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Tracer

Summary This study deals with solute transfer in the vertical continuum between the unsaturated zone and shallow groundwater of a weathered granite aquifer in the Kerbernez headwater catchment of western France. The objectives are (i) to determine the mechanisms responsible for solute transfer in the unsaturated and water-table fluctuation zones of the aquifer, and (ii) to analyse the implications of these results on solute transfer times at the catchment scale. An experimental site located in the plateau area of the catchment was equipped with 6 tensiometers, 18 ceramic cups at depths from 0.25 to 2.5 m and 7 piezometers from 3 to 20 m. Measurements of hydraulic head and water sampling were carried out over a period of 2.5 years in the unsaturated zone (0—2 m), the water table fluctuation zone (2—9 m) and the permanently saturated zone (>9 m). Two tracer experiments were carried out by applying two pulses of water, one enriched with deuterium and the other with bromide. Natural chloride concentrations, as well as deuterium and bromide concentrations, were analysed from solution samples. From the artificial tracer concentrations, two porosity compartments can be identified and partly quantified: (1) the slow-mobile porosity (36% of the bulk volume), accounting for the slow piston-flow transfer (2—3 m per year), and (2) the rapid-mobile porosity, which transfers small quantities of bromide at a rate of 19 cm h^{-1} down to the water table. Natural

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chloride concentrations are characterised by a high temporal variability in the water-table fluctuation zone, whereas the concentrations remain steady in time in the permanently saturated zone (42 mg l^{-1} at 20 m depth). The temporal variability is related to the water-table fluctuations and follows the same pattern each hydrological year, i.e. low concentrations during rising water-table followed by a progressive increase in concentrations during the periods of high piezometric level and water-table recession. This pattern is explained in terms of the two mobile porosity compartments and groundwater hydraulics. Based on these findings, we propose a conceptual model of solute transfer along the hillslope of a headwater catchment. We conclude that mixing in the water-table fluctuation zone could occur at two spatial scales. Firstly, at the pore scale, with mixing of waters in slow mobile and rapid mobile porosity, and secondly, at the scale of the hillslope. The mixing at this latter scale would appear to result from differences of flow path geometry and velocity between the unsaturated zone and the groundwater.

Introduction

In watershed underlain by crystalline bedrock, most of the solutes and water fluxes in the stream come from shallow groundwater that accumulates above and within the fractured crystalline bedrock. One of the key characteristics of the hydrology and hydrochemistry of these catchments is that the stream flow and water-table variations are highly reactive to rainfall, whereas the solute concentrations remain steady in time or are strongly damped in the streams and the deep groundwater (Kirchner et al., 2001; Molenat et al., 2002; Martin et al., 2004). Recent reviews have indicated that solute transfer in headwater catchments are characterised by wide time scales ranging from days to years, and that we require a better understanding of the flow paths and transfer mechanisms involved on such time scales (Mc Donnell, 2003; Kirchner, 2003). Furthermore, Kirchner (2006) underlined the need for a better temporal resolution as well as spatial resolution to analyse correctly solute transfer.

Although groundwater recharge is a key link in the transfer of solutes from the soil surface to streams, the process is still poorly understood, particularly in the interaction between the unsaturated zone and the groundwater. These two zones have generally been analysed separately. Most studies focusing on groundwater recharge assume that groundwater chemistry depends only on the solute concentration and volume of water reaching the water table (Landon et al., 2000; De Vries and Simmers, 2002). In the same way, classical transport models assume that, once the water and solutes have reached the water table, they are completely and instantaneously mixed with the pre-event groundwater (Beaujouan et al., 2002; Wade et al., 2002). However, in recent studies, Silliman et al. (2002) and Berkowitz et al. (2004) pointed out that a steady water table is a highly active and complex zone in terms of water and solute mixing. These processes include not only vertical flow from the recharge but also lateral flow from upslope. Moreover, little field evidence is available to support the assumption of complete and instantaneous mixing between water flowing vertically from the unsaturated zone and pre-event groundwater. Such an assumption is therefore highly questionable, and all the more so in catchments such as those in Western France where the free groundwater surface is often very reactive to rainfall and exhibits large fluctuations within the weathered material on the year scale (Martin et al., 2004; Molenat et al., 2005). Weathered material differs from other multiporosity materials such as soils, since it retains much of the structure and regularity of the bedrock, including rapid flow through relict fractures (Van Der Hoven et al., 2003) and variable exchanges between the different porosity compartments. Currently, little is known about the water and solute transfer in such materials, as well as the mixing processes involved. Generally speaking, we do not have a good understanding of the impact of variably saturated conditions, such as those induced by water table fluctuations, on flow and solute transfer processes (Hinz, 1998; Sinke et al., 1998).

In this paper, we focus on vertical solute transfer in the unsaturated zone-groundwater continuum of a weathered granite aquifer in a headwater catchment. The study aims at assessing the water flow and solute transfer processes occurring above, at and below the water table. For this purpose, we carried out a field investigation to (i) determine the mechanism responsible for solute transfer in the unsaturated and water-table fluctuation zones, and (ii) analyse the implications of these results on solute transfer times at the catchment scale. The experimental site is located in the Kerbernez catchment, western France. The arrangement of instruments on this site allows water sampling and the measurement of hydraulic head at various depths in the unsaturated zone, the water table fluctuation zone and the permanently saturated zone of the aquifer. Solute transfer was analysed by monitoring natural chloride concentrations and performing two tracer experiments.

Materials and methods

The Kerbernez catchment

The Kerbernez catchment, previously described by Ruiz et al. (2002) and Martin et al. (2004), is located in southwestern Brittany (Fig. 1a). It is an agricultural headwater catchment covering an area of 0.12 km^2. The climate is oceanic with a mean annual precipitation of 1167 mm over the last decade (Standard deviation, SD = *195 mm*) and a mean annual Pennman potential evapotranspiration (PET) of 616 mm (SD = *71 mm*). Kebernez is an headwater catchment where runoff in excess of saturation occurs locally in the valley bottom when groundwater is at the soil surface. In

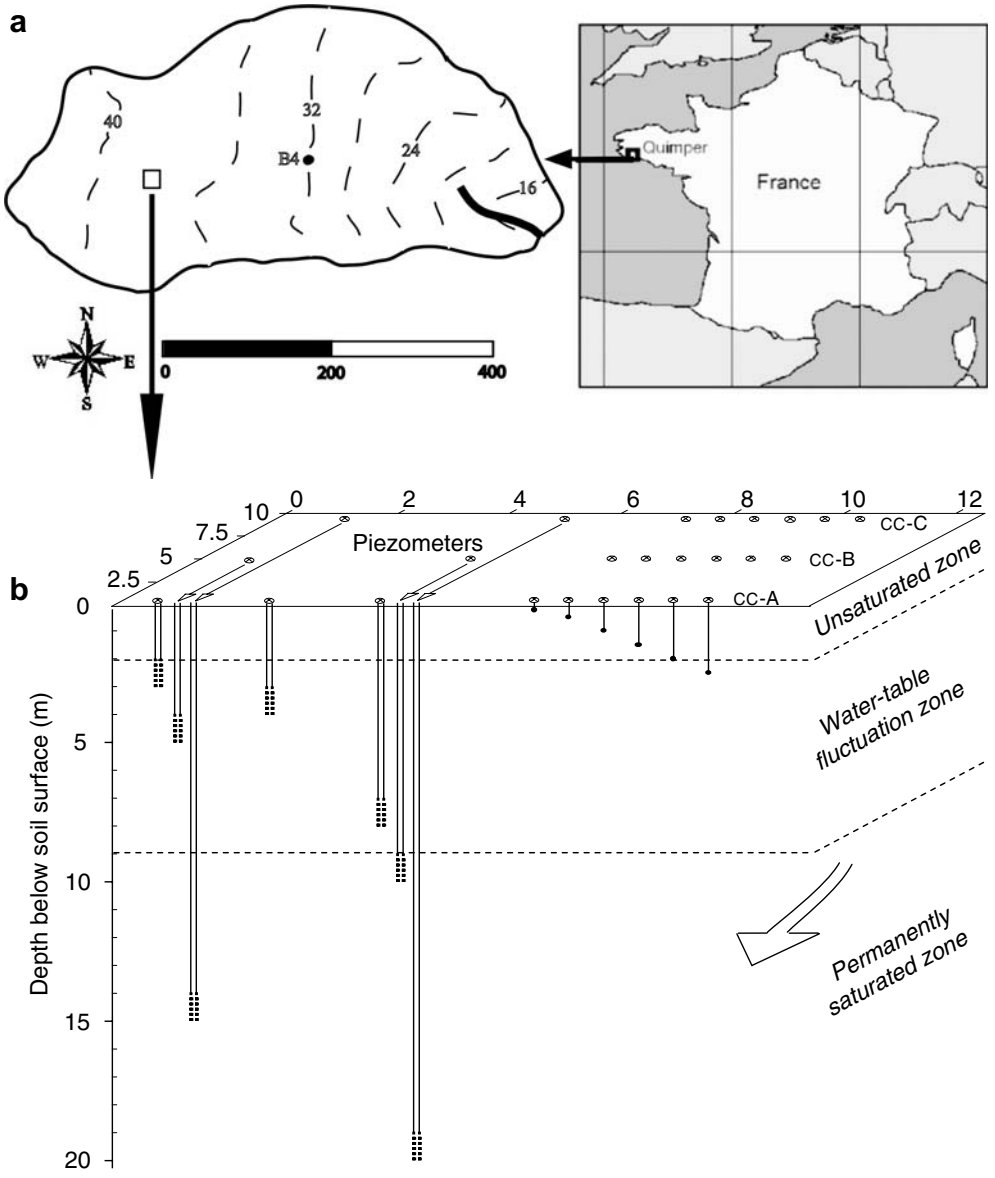

Figure 1 Location and map of the Kerbernez catchment (a) with the experimental arrangement (b). (a) The dashed lines on the map are topographic contours with values in metres above sea level. The bold line represents the stream. B4 is a 15-m deep piezometer used by Martin et al. (2004). (b) All units on *x*-, *y*- and *z*-axes are in metres. The dashed lines at the base of each piezometer correspond to the perforated screen section allowing the sampling of water from a 1-m thick groundwater layer. The three profiles of six ceramic cups are also indicated as cc-A, cc-B and cc-C. The two horizontal dashed lines at 2 m and 9 m shows the maximum and minimum levels reached by the water-table. The arrow indicates groundwater flow direction.

the upslope part of the catchment, there is almost no runoff in excess of infiltration.

The bedrock is a fissured and fractured granite, overlain by weathered material. The weathered granite constitutes the aquifer within which the shallow groundwater develops. The groundwater is unconfined and exhibits a free and highly fluctuating water table. The thickness of the weathered granite varies from 1 to more than 20 m, as shown by electrical imaging surveys (Legchenko et al., 2004). The weathered granite lies at between 0.7 and 1.2 m below the soil surface. The soils are mainly sandy loam (Dystric Cambisol, FAO Classification). The weathered granite exhibits facies with different colours, textures and structures as observed in a 20-m-long trench close to the 120 m^2 experimental site:

- white weathered granite with a destroyed structure (*Gw*),
- red weathered granite with a destroyed structure (*Gr*),
- weathered granite with a preserved structure (*Gs*),
- 1-cm wide and 1-m spaced sub-vertical red fingering facies existing in *Gw* (*Gf*),
- 10-cm wide and 10 m spaced sub-vertical and sub-horizontal quartz veins (*Qv*).

The first three facies (*Gw*, *Gr* and *Gs*) are juxtaposed weathered granite blocks, considered as representing the weathered granite matrix. The *Gf* and *Qv* facies correspond to geological discontinuities such as fissures or fractures (Legout et al., 2005). The textural properties and bulk densities of the different facies are reported in Table 1. The experimental bulk density values are used to determine the mean porosity of the weathered granite as follows:

$$\text{Porosity} = 1 - (D_b/D_p) = 0.42, \quad (1)$$

where D_b is the mean bulk density of the weathered granite matrix (1.55 g cm^{-3}) and D_p the particle density (2.65 g cm^{-3}).

The experimental arrangement

In November 2001, a 10 × 12 m plot was equipped in the plateau area (Fig. 1) for sampling water in the vadose zone and in the groundwater. This plot is located in a grassland under pasture since 1996. Three profiles of 6 ceramic cups at 25, 50, 100, 150, 200 and 250 cm depth below the soil surface (Fig. 1b) were used to collect water samples in the vadose zone by applying a depression of 0.6 bar for 24 h. The ceramic cups were put in place using a hand auger with a diameter slightly smaller than the diameter of the ceramic cups. The soil and weathered granite were not disturbed by the emplacement. The groundwater samples were collected through 7 piezometers penetrating to 3, 4, 5, 8, 10, 15 and 20 m below the soil surface (Fig. 1b). The 15 and 20 m piezometers correspond to the B5A-B wells reported in Fig. 1 in Martin et al. (2004). Data for the 3, 4 and 8 m piezometers are only available for the 2003/2004 hydrological year. The piezometers were made of PVC tubes with a 1-m long perforated screen section at their base, allowing the collection of water from a 1-m thick groundwater layer. With this arrangement, the water collected in each piezometer is strictly representative of the groundwater at the piezometer depth. The annular space around the tube was backfilled with gravel up to 1.5 m from the base of the tube. A bentonite seal was placed immediately above the gravel layer, and the rest of the annular space was filled with weathered granite and a 2-m thick layer of cement up to the soil surface. This experimental arrangement allowed us to characterise the water chemistry at different depths in three distinct layers of the aquifer, i.e. the unsaturated zone, the water-table fluctuation zone and the permanently saturated zone (Fig. 1b).

Hydrochemical measurements and methods

The sampling frequency in the vadose zone and in the groundwater varied between weekly to monthly during the recharge period and the summer, respectively. The water samples were filtered in the field with 0.2 μm polytetrafluoroethylene (PTFE) membranes before storing. They were stored for less than 24 h in the dark below 4 °C and analysed for chloride and bromide concentrations by ionic chromatography (Dionex DX 100). The quantifying limits were 0.1 and 0.05 mg l^{-1} for chloride and bromide concentrations, respectively.

Hydrometric measurements were also performed. The pressure potential of water in the vadose zone was measured by tensiometers at depths ranging from 0.25 to 2.50 m below the soil surface, with a weekly to monthly frequency. Water content in the weathered granite at a depth of 1 m was estimated by the gravimetric method using the same sampling frequency from March 2003 onwards. Cores were sampled and weighed before and after being oven dried at 105 °C. The groundwater levels were measured automatically in piezometers and recorded by data loggers every 15 min. An automatic weather station, located near the site, recorded the hourly rainfall and other variables necessary to estimate the daily PET from Penman's formula.

The daily percolation flux to the groundwater was calculated as the difference between rainfall and PET when this difference was greater than zero, and otherwise taken as zero (Fig. 2a). This assumption is realistic since all the rainfall infiltrates and almost no runoff occurs in excess of infiltration in the upslope part of the Kerbernez catchment. However, such an estimation of the percolation flux leads to overestimation of the real percolation flux. This is because we do not take account of the drying of the soil during periods where the potential evapotranspiration is higher than rainfall. Since the climate is oceanic and the daily PET does not exceeds a few millimetres (median value of 1.3 mm with a maximum of 6 mm), we assume that this calculation of percolation flux is realistic. Nevertheless, we emphasize that the porosities calculated from the long-term tracer transfer may be slightly over-estimated. These porosities correspond to the ratio between the daily cumulative

Table 1 Textural properties and densities for the different weathered granite facies (*Gr*: red granite with a destroyed structure; *Gw*: white granite with a destroyed structure; *Gf*: red fingering zones; *Gs*: facies with a preserved structure)

	Gr	Gw	Gs	Gf
Textural properties (%)				
Clay (0–2 μm)	6.9 (2.3)	4.4 (2.9)	1.8 (0.1)	9.7 (3.6)
Fine silt (2–20 μm)	7.1 (3.2)	7.6 (5.7)	1.1 (0.2)	11.6 (1.4)
Coarse silt (20–50 μm)	5.5 (2.1)	4.8 (3.0)	1.0 (0.3)	7.1 (0.5)
Fine sand (50–200 μm)	9.9 (2.6)	8.9 (4.2)	3.0 (0.4)	13.8 (4.0)
Coarse sand (200–2000 μm)	70.7 (9.3)	74.4 (15.3)	93.0 (0.1)	57.7 (2.5)
Bulk density (g cm^{-3})	1.5 (0.0)	1.4 (0.1)	1.7 (0.1)	–

Values in brackets are standard deviations.

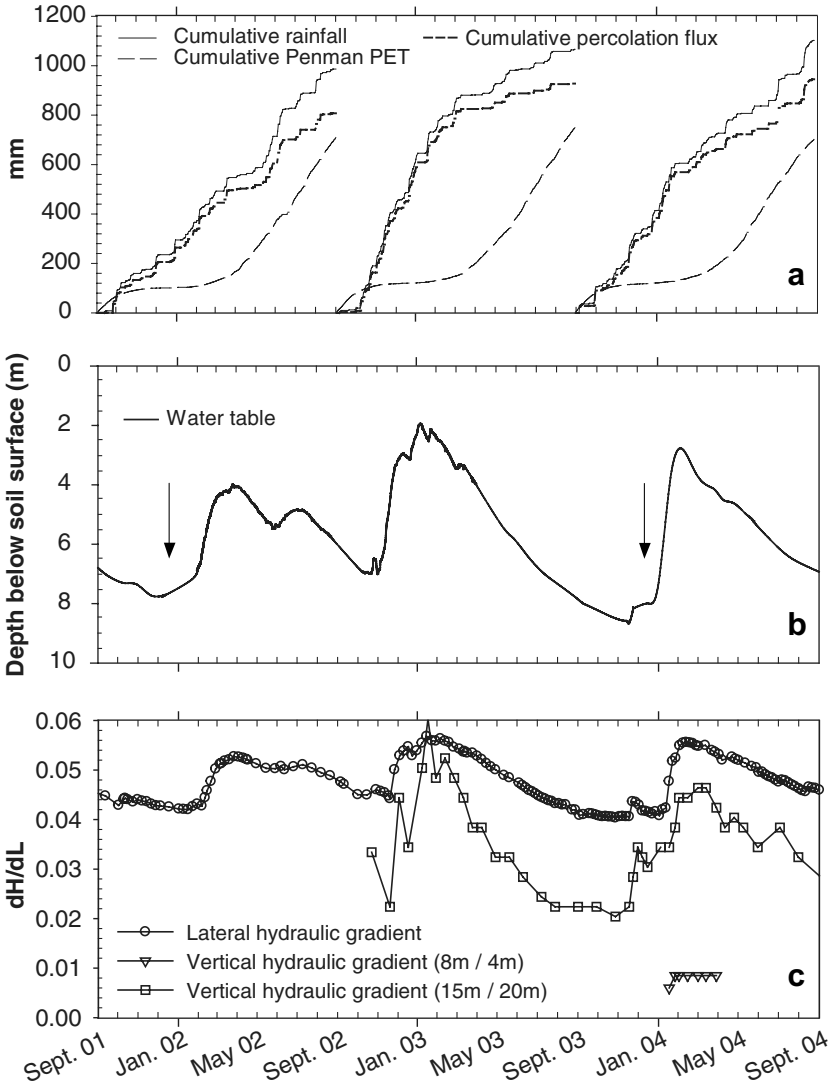

Figure 2 (a) Cumulative rainfall, potential evapotranspiration and percolation flux. (b) Water-table fluctuations measured from the 20-m deep piezometer located in the 10×12 m plot in the plateau area. Black arrows indicate the dates of each tracer application. (c) Lateral and vertical hydraulic gradients.

percolation flux since tracer application and the depth in millimetres of the tracer peak.

Tracer experiments

A first tracer experiment was started on 20th December 2001, using 2.5 mm of a deuterium-enriched solution ($\delta D_{Sp} = 6200‰$) applied over the whole plot area of 120 m^2. To obtain a homogeneous application of the tracer, the 10×12 m plot was divided up into 50-cm wide lanes and the deuterium solution was sprinkled with a watering can. During the year following this application, part of the water collected for anion analysis in the vadose and saturated zones was used to perform isotopic measurements. Water samples were stored in the dark below 4 °C, but not filtered at 0.2 μm. The isotope concentrations (^{18}O, ^{2}H) were analysed and expressed as δ (‰) values, the deviation of the concentration in parts per thousand from the Vienna Standard Mean Ocean Water (V-SMOW). According to Craig (1961), the natural concentration of deuterium (δDN) is linearly correlated with the concentration of oxygen 18 ($\delta^{18}O$):

$$\delta D_N = 8\delta^{18}O + 10. \quad (2)$$

In order to correct the deuterium measured values for the natural temporal variation of rainwater deuterium values, we define the deuterium excess (δD_E) as the difference between the δD values measured from our water samples and the results from Eq. (2). The δD_E values are then interpreted as the enrichment produced by the spraying of deuterium solution.

A second tracer experiment was started on 18th December 2003 by applying 2.5 mm of a bromide-enriched solution (2 g l^{-1}). We used the same spraying protocol as explained above for the deuterium. In addition to the weekly sampling, we also performed high-frequency sampling during the 120 days following the tracer application to investigate transfer mechanisms at the storm-event scale. For this purpose, two automatic samplers were used to collect water

every 15 min at the water table and 2 m below the water table. As the water table fluctuated, the samplers were moved from one piezometer to another in order to stay as close as possible to the same configuration, i.e. one sample in the first 50 cm below the water table and another sample 2 m below the water table. The mass recovery was calculated for the bromide experiment at each sampling date following the application. No recovery was calculated for the deuterium experiment as no moisture content date was available during the few months following the application. The bromide mass recovery, R, was estimated according to

$$R = \sum_{i=1}^{6} [\mathrm{Br}]_i * V_i * \theta_i / M_{\mathrm{Br}}, \quad (3)$$

where $[\mathrm{Br}]_i$ is the bromide concentration in the layer i, with i comprised between 1 and 6 corresponding to the 6 ceramic cups depths, V_i the volume of the considered layer, θ_i the moisture in that layer and M_{Br} the total mass of applied bromide, i.e. 5 g m^{-2}. For each date, the range of the mass recovery was estimated from the bromide concentration variability between the replicates, i.e. between profiles A, B and C, and from the moisture variability obtained from the 3 soil samples replicates.

Results

Hydrology

Over the whole study period, the water-table fluctuated in a range from 1.9 to 8.8 m below the soil surface (Fig. 2b). During the 2003/2004 recharge period, the water-table variation reached 6.2 m, ranging between a minimum level of 8.8 m below the soil surface (19th November 2003) and a maximum level of 2.6 m below the soil surface (31st January 2004). During this 73-day period, the cumulative daily percolation flux was 390 mm. The water-table variation reached a maximum between the 1st January 2004 and the 31st January 2004 with a rise of 5.8 m for a cumulative daily percolation flux of 185 mm. The ratio between the cumulative daily percolation flux and the water-table elevation corresponds to the specific yield, which, in this 30-day period, can be calculated as 3%.

The lateral hydraulic gradient was calculated from the difference in hydraulic head, dH, between the 20-m deep piezometer located in the 10 × 12 m plot in the plateau area and another 15-m deep piezometer located in the midslope domain of the catchment (labelled B4 in Fig. 1a). These gradients range from 4% to 5.8% in the upslope part of the hillslope, as shown in Fig. 2c. The temporal variations in lateral hydraulic gradient follow the same pattern as the water-table fluctuations, with the highest gradients observed during the peaks of groundwater rise and the lowest in summer when the water table is deeper. The vertical hydraulic gradient, calculated from the difference in water-table depth between two nearby piezometers located approximately on the same topographic contour, show values ranging from 2% to 6% between the two deepest piezometers (at 15 m and 20 m). These vertical gradients exhibit temporal variations through the hydrological year reflecting the water-table fluctuations. As indicated in Fig. 2c, the vertical hydraulic gradients are very weak between the shallow piezometers (at 4 m and 8 m) during periods of high water-table.

Chemistry

Data on the water chemistry of samples collected from the ceramic cups shows that chloride concentration is highly variable in time and space. Chloride concentration is lower in the soil (mean value of 8 mg l^{-1} at 1 m depth) than in the upper part of the weathered granite (mean value of 15 mg l^{-1}). Within the upper part of the weathered granite a wide range of chloride concentration is also found, from 3 to 60 mg l^{-1} at 1.5 m. In groundwater, chloride concentration is high, with mean values of 36 and 42 mg l^{-1} for the 15-m and 20-m depth piezometer, respectively, and almost steady in time. By contrast, mean anion concentration in the shallowest piezometers tend to be lower and exhibit a great time variability of chloride concentration, ranging from 8 to 39 mg l^{-1} in the 5-m depth piezometer.

Considering the time variability of groundwater chemistry just below the water table, we have separated the hydrological year into three periods, namely: (a) *the water-table rise period* characterised by a decrease of the chloride concentrations, (b) *the high piezometric level period* exhibiting a significant increase of the concentrations, and (c) *the water-table recession period* during which chloride concentrations were much steadier. We observe that the mean chloride concentrations increase with depth below the water table during periods a and b (Table 2). Meanwhile, the standard deviations and 10–90% percentiles show that the variability in chloride concentrations decreases with depth below the water table. Furthermore, this variability is higher during periods a and b than period c.

Results from the deuterium (Fig. 3a) and bromide (Fig. 3b) tracer experiments show a high spatial variability, especially in the weathered granite below 1 m depth. Indeed, the differences in δD_{E} or bromide concentration can be higher between two neighbouring ceramic cups at 2 m depth than between two ceramic cups at depths of 1 m and 2 m. The values of the peaks decrease with depth, especially in the topmost metre, with $\delta D_{\mathrm{E_{max}}}$ and $\mathrm{Br}^-_{\mathrm{max}}$ falling by a factor of two between 25 cm and 100 cm below the soil surface. For each sampling depth in the vadose zone, the δDE and Br^- values increase progressively and show a shift with time as depth increases (Fig. 3).

The relationship between occurrence time of tracer peak (x), expressed as the cumulative percolation flux since tracer application, and profile depth (y) is linear for the two tracers ($y = 2.8x$, $R^2 = 0.86$ for deuterium and $y = 2.7 \times$ with $R^2 = 0.73$ for bromide). This approach, based on the most representative velocity of tracer transfer and called the peak-migration method by Joshi and Maulé (2000), yields a mean solute transfer velocity of 2.8 and 2.7 mm per mm of daily percolation flux in the first 2.5 m below soil surface for deuterium and bromide, respectively. Since cumulative daily percolation flux was 1056 and 812 mm during the year following the tracer application for the deuterium and the bromide experiments, respectively, this yields a mean velocity of displacement of 2.5 m per year. These values are considered as the average velocity of transport in the upper 2.5 m of the soil and weathered granite profile. The

Table 2 Chloride concentrations of the bulk water samples collected from piezometers since December 2001

Depth below water table (m)	Period	Number	Mean	Std. Dev.	10% percentile	90% percentile
0—2	a	18	26	14	10	41
	b	16	25	8	14	37
	c	7	38	4	33	44
2—5	a	17	31	10	17	40
	b	11	28	7	18	36
	c	13	38	3	34	42
5—10	a	27	35	6	21	40
	b	25	35	7	23	42
	c	9	38	2	35	42
>10	a	34	40	3	35	44
	b	38	39	4	35	43
	c	17	40	3	34	43

The statistical parameters are considered at different depths below the water table for three periods: (a) water table rise, (b) high piezometric level, and (c) water table recession. The number column gives the number of samples analysed for each period within each depth range.

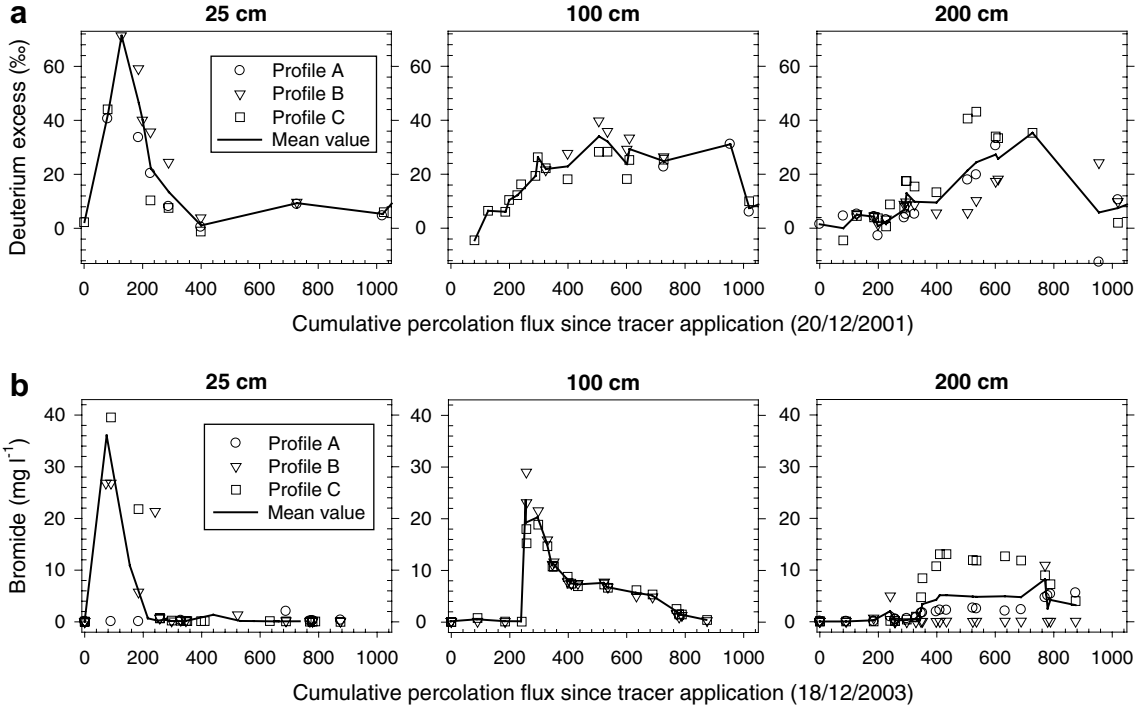

Figure 3 Tracer experiments with (a) deuterium and (b) bromide. The tracer concentrations are indicated for each water sample collected at various depths from the cc-A, cc-B and cc-C profiles of ceramic cups. The thick lines correspond to variations of the average values from the three ceramic cups at each depth. The deuterium and bromide-enriched solutions were sprayed on the 20th December 2001 and on the 18th December 2003, respectively.

dispersion around this mean velocity varies and increases with depth as shown by the spreading over time of the breakthrough curves (Fig. 3).

For the bromide tracer experiment, we observe a significant increase of bromide concentration above the background concentration of around 0.17 mg l^{-1} at the groundwater table, whereas no increase is recorded deeper in the groundwater (Fig. 4c). The bromide concentrations started to increase 22 h after the tracer application. Since the water table was 7.6 m below the soil surface at this period, the associated maximum velocity of bromide transfer was 35 cm h^{-1}. The peak of bromide concentration was reached 40 h after the tracer application, which corresponds to the first rainfall event (3 mm between the 39th

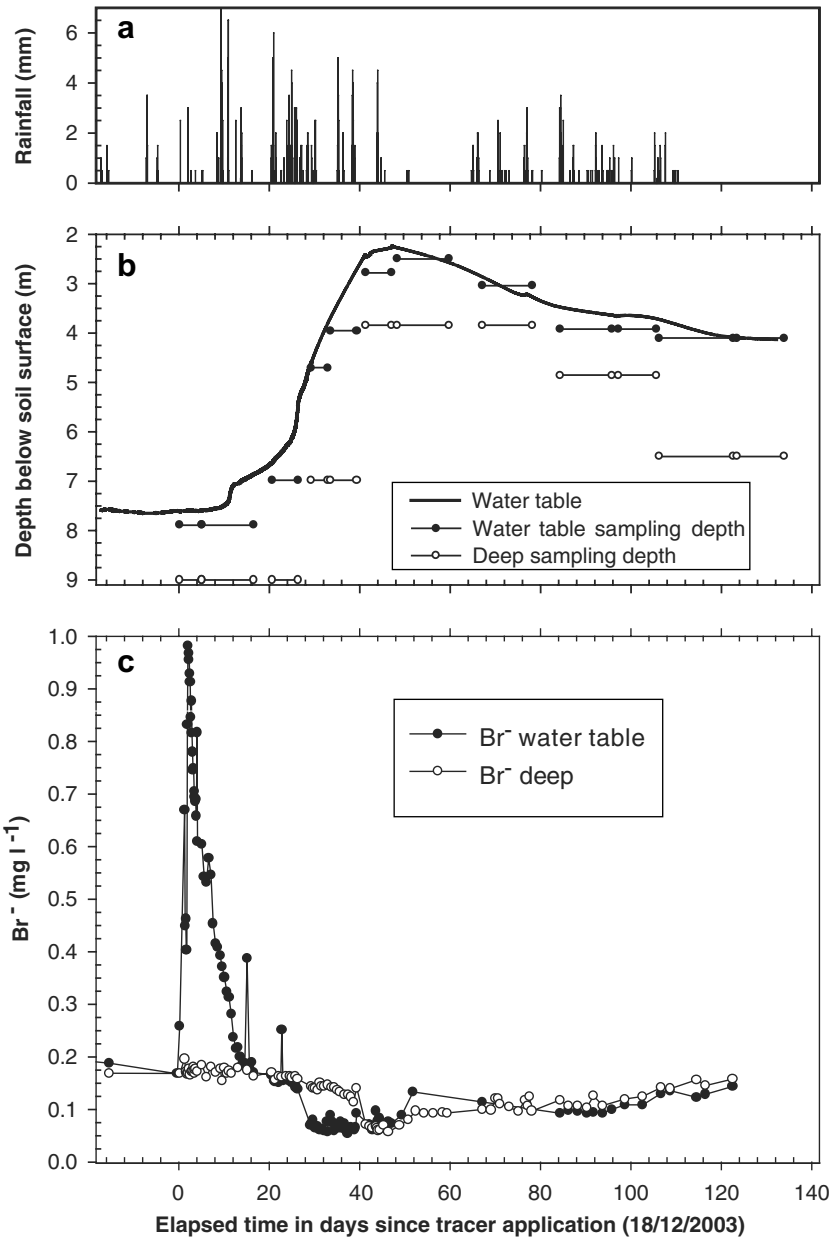

Figure 4 Bromide tracer experiments. (a) represents the hourly rainfall. (b) shows the water-table fluctuations with sampling depth for each groundwater sample collected at the water table and deeper in the groundwater. (c) Bromide concentrations at the water table and deeper in the groundwater.

and 40th hour) following the tracer spraying (mean velocity of transfer of 19 cm h^{-1}). The decrease of bromide concentration was then progressive over 18 days, implying a minimum transfer velocity of the bromide tracer of around 2 cm h^{-1}. The bromide concentrations returned to their initial level 20 days after the tracer application and continued to decrease down to 0.05 mg l^{-1} 30 days after the tracer application. By contrast, we observed no enrichment in deuterium in the groundwater following the spraying of deuterium-enriched solution at the soil surface. However, the sampling frequency in the groundwater was not appropriate for observing the rapid inflow of spiked water. Moreover, the deuterium tracer was applied on a soil-weathered granite profile far from saturation (capillary potential $h_{25\,cm} = -121$ cm and $h_{150\,cm} = -75$ cm) when compared with the bromide tracer experiment ($h_{25cm} = -37$ cm and $h_{150\,cm} = -37$ cm), which could have led to smaller amounts of tracer undergoing rapid transfer.

The mean rainfall chloride concentration is 10 mg l^{-1} (SE = 2) during the study period. The rainfall chloride concentrations are highly variable from one rainfall event to another, ranging from 2 to 47 mg l^{-1}, but the mean concentration does not vary significantly between years. In the topmost 2 m below the water table, the groundwater chloride concentrations are highly variable, with minimum values related each year to high piezometric levels (Fig. 5). The chloride concentrations in the deep permanently saturated zone (20 m depth) remain almost steady on the timescale of a

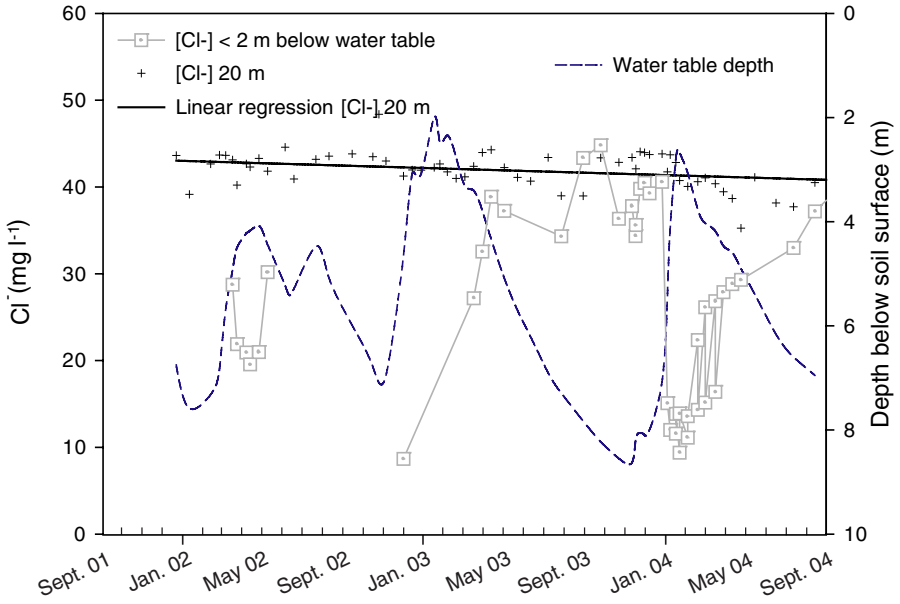

Figure 5 Temporal variation of chloride concentrations since 1st September 2001 in rainwater, in samples collected from the 2.5-m deep ceramic cups, in samples from the topmost 2 m below the water table and from the 20-m deep piezometer. A linear trend is represented for a depth of 20 m ($Y = -0.002X + 43.2$ with a correlation coefficient $R = 0.38$).

year, while decreasing slightly during the study period at rates lower than 1 mg l^{-1} per year according to the linear trend indicated in the caption of Fig. 5.

Discussion

Pathway and transfer velocity in the variably saturated weathered granite

In order to analyse solute transfer in the weathered granite, we need to divide the porosity of the aquifer into two compartments: (1) the slow-mobile porosity, in which most of the solutes are transferred slowly by convective flux and (2) the rapid-mobile porosity, responsible for the short-term penetration of water through distinct pathways traversing the vadose zone and bypassing most of its volume.

In the unsaturated zone of the aquifer, most of each tracer moved vertically through a slow-mobile porosity compartment, leading to variations in solute concentrations at a longer time scale than the rainfall event. Two evidences support this long-term transport. Firstly, the major part of the applied mass tracer remained in the 3 m top layer of the soil and weathered granite profile and did not leave this layer in the year following the tracer application. This is clearly shown by the values of mass recovery calculated for the bromide experiment. Indeed, even if the range of variations is large, the average bromide mass recovery, R, in the 3 m top layer was 0.92 ($0.64 < R < 1.16$) in January 2004 (after 92 mm of rainfall), 0.79 ($0.49 < R < 1.14$) in February 2004 (after 264 mm of rainfall) and 0.61 ($0.29 < R < 1.16$) in September (after 766 mm of rainfall). Secondly, considering the peak of tracer as an indication of the mean velocity of transport, the average distance of tracer displacement over a year after application was short: 3 m for the deuterium and 2 m for the bromide. Expressed as a function of the percolation flux, the velocity of the two tracers was very close with 2.7 mm and 2.8 mm of displacement per 1 mm of percolated water for bromide and deuterium, respectively. The similarity between the two velocities suggests that tracer movement in the unsaturated zone of the aquifer depends mainly on the cumulative percolation water flux. Furthermore the inverse of the average velocity corresponds to the size of the slow-mobile porosity compartment, leading to 36% of the bulk volume for the deuterium experiment and 37% for the bromide experiment. As the percolation flux we used are overestimated, these porosities can also be considered as an overestimation. Nevertheless, these estimations are in accordance with the maximum water contents (39% recorded at 1-m depth in the unsaturated weathered granite). Since the total porosity of the weathered granite is around 42%, of the bulk volume, the slow-mobile porosity compartment is the main porosity compartment in terms of relative volume.

The cumulative percolation flux is the main control on the average tracer displacement in the unsaturated zone at the year scale. However, for the deuterium, the velocity was not fully steady along the profile as it moved slower in the upper 1 m and faster below 1 m. The variations might be related to rainfall conditions and hydraulic gradient variations following the deuterium application as hydraulic gradients were highly variable in the upper 1 m during spring 2002, indicating alternative periods of downward and upward water flow. This hydraulic gradient variability might have slowed down the deuterium displacement in the upper 1 m of the unsaturated zone. By contrast, no significant upward flux were observed neither below 1 m depth during the whole study period, nor in the topsoil layer after bromide application (winter and spring 2004). This may be the reason

why the bromide average velocity of transport remained steady along the uppermost 3 m.

So far we have showed that the two tracer displacements can be characterised by an average velocity that depends on cumulative percolation flux. However, displacement is also characterised by a wide range of flow velocities around this average value, as shown by the spreading over time of the deuterium and bromide breakthrough curves at various depths in the unsaturated zone (Fig. 3). The spreading over time of the concentrations indicates also that the tracer displacement diverges from a pure piston-like flow.

The high variability of the velocities can have two origins: The first one is the hydrodynamic dispersion related to the heterogeneity of the slow mobile porosity. Hydrodynamic dispersion theories suggest increased dispersion with velocity and this could partly explain why was dispersion of deuterium larger than bromide (Fig. 3) since the velocity of the former was larger than that of the latter (3 m/year and 2 m/year, respectively). The second origin of concentration spreading could be diffusion. Actually diffusion in soil can displace significantly the tracer in two distinct ways: (a) between mobile and immobile water and (b) within mobile water when convection is low. The role of immobile water on denitrification has already been pointed out by Legout et al. (2005). The fraction of immobile water can not be quantified from our experiments. Diffusion within mobile water must not be significant in tracer displacement most of the time. In the Kerbernez catchment percolation flux was well distributed during the hydrologic years 2001–2002 and 2003–2004 as indicated by the continuous increase of cumulative percolation flux (Fig. 2a). As percolation flux drives the solute displacement by convection, tracer is more likely to be displaced by convection than by diffusion. Only during the end of the hydrologic year 2002–2003, displacement by diffusion in mobile water could have been significant since percolation flux was very low at this period (Fig. 2a).

The high-frequency groundwater sampling after bromide application reveals that small quantities of tracer were transferred rapidly at mean velocities of 19 cm h^{-1} (ranging from 2 to 35 cm h^{-1}) down to the water table (Fig. 4). During natural conditions, a fraction of the rainfall is also likely to move rapidly from the soil surface through the unsaturated zone down to the water table. The applied tracer flux involved in the rapid displacement is difficult to estimate. Two evidences indicate that rapid flux did not exceed 10–15% of the applied flux. The first evidence is the mass recovery. More than 90% of the bromide remained in the uppermost metre after 92 mm of rainfall. The second evidence comes from the water table rise following the application. The water table rise during the two days following the application was 1 cm. Assuming that this rise can be attributed to a fraction of the 2.5 mm enriched solution moving rapidly and that the specific yield is 3%, only 12% of the applied tracer was transferred rapidly down to the water table.

The rapid arrival of the bromide peak at the water table allows us to highlight three points: (i) the progressive disappearance of the bromide pulse from the water table, (ii) the absence of an increase in bromide concentration at 9 m depth in the days following the tracer application and (iii) the decrease of bromide concentration below its initial level of 0.17 mg l^{-1} at the water table 26 days after the tracer application, and also 3 m below the water table, in the 8-m piezometer, 40 days after the tracer application (Fig. 4c). This latter feature coincides with the decrease of 12 mg l^{-1} in the chloride concentration at 8 m depth during this period of high percolation flux (Fig. 6). According to these results, we could infer that the bromide-rich water mixes with pre-event groundwater from the slow-mobile porosity before reaching a depth of 9 m. We may also assume that the bromide concentration peak was transferred laterally rather than vertically within the groundwater body, since the lateral hydraulic gradients were at least as high as the vertical gradients (Fig. 2c), leading to flow in a sub-horizontal direction. In any case, the leaching of the bromide peak as well as the decrease in chloride concentrations is necessarily related to the rapid influx of solute-poor rain water at the water table.

In this study, we have identified two porosity compartments based on a functional approach considering two types of porosity in the weathered granite. In the rapid-mobile porosity, the percolating water is transferred to the groundwater rapidly within a few hours following the rainfall event. In the slow-mobile porosity, the water percolates slowly into the groundwater at an average velocity of 2–3 m per year. While it is often difficult to relate functional definitions to physical properties, we attempt here to link the porosity compartments to the morphological properties of the weathered granite. The *Gw*, *Gr* and *Gs* facies observed in the field are mainly sandy (Table 1), exhibiting a matrix porosity that appears to be continuous with few visible macropore networks. From this, we can assume that the slow-mobile porosity compartment is spatially distributed mostly in the weathered granite matrix, i.e. in the *Gw*, *Gr* and *Gs* facies. By contrast, we observe large pores in the *Gf* and mainly in the *Qv* facies. Consequently, rapid flow is more likely to occur in one or both of these two latter facies.

Chemical variability in the water-table fluctuation zone

We note two striking results from the observations on groundwater chemistry. Firstly, there is a high temporal variability in chloride concentrations just below the groundwater surface, whereas the concentrations remain almost constant at greater depth (Fig. 5). Secondly, the temporal variability of concentrations in the shallow piezometers (3, 4, 5 and 8-m deep) occurs at a larger scale than the rainfall event and follows a similar pattern in winter from one year to another. The behaviour is characterised by low concentrations when the water table first begins to rise, followed by a progressive increase in concentrations (Fig. 6c). As reported in Table 2, the largest variations in chloride concentration are observed in the topmost 2 m below the water table during the period of rising water-table. Variations of the concentrations associated with water-table fluctuations have also been observed in the groundwater of chalky aquifers over much of southern and eastern England (Fretwell et al., 2005) and in Belgium (Brouyère et al., 2004).

In the following, we show that the variability of groundwater chemistry in the water-table fluctuation zone can be

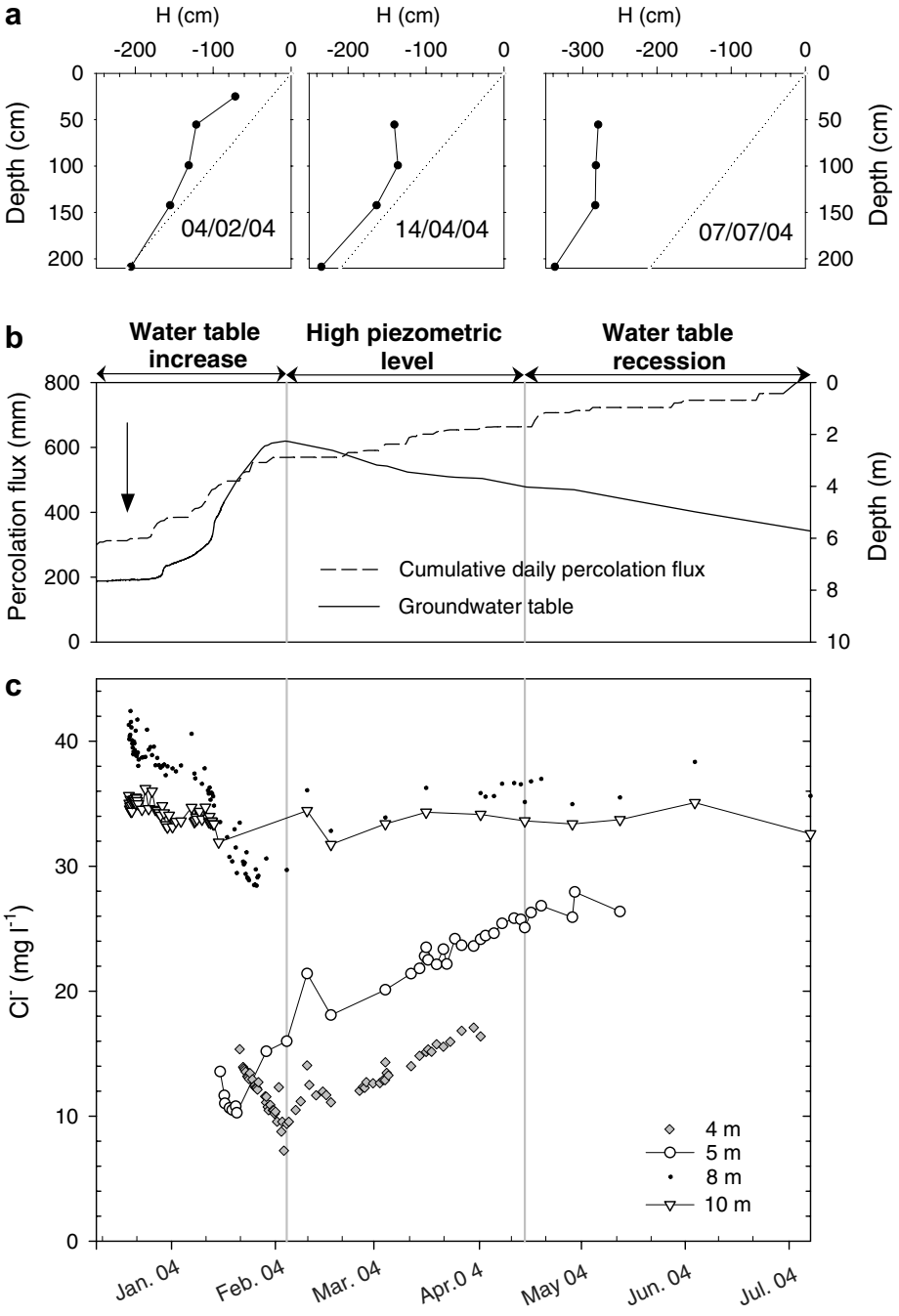

Figure 6 Separation of the three characteristic periods of water-table rise, high piezometric level and water-table recession in terms of (a) hydraulic head profiles, H, where the dotted lines correspond to gravity head profiles, (b) percolation flux and groundwater table depth with a black arrow indicating the date of the bromide application and (c) temporal variations of chloride concentrations in the 3, 4, 5, 8 and 10-m deep piezometers.

explained by considering the two porosity compartments identified above as well as the hydraulics of the groundwater. With this objective in mind, we need to distinguish three periods: water-table rise, high piezometric level and water-table recession (Fig. 6c).

Period (a) — water-table rise

At the beginning of this period, the chloride concentrations close to the water table (in the 8 and in the 10-m deep piezometers) remain steady at around 40 mg l^{-1}. As the rainfall percolates, the unsaturated zone becomes very close to saturation as shown by the hydraulic head profile on the 4th February 2004 (Fig. 6a). Hence, the slow-mobile porosity compartment may be close to saturation. When the rainfall rate exceeds the hydraulic conductivity of the slow-mobile porosity, the chloride-poor rainwater percolates into the rapid-mobile porosity. This chloride-poor water is transferred rapidly down to the water table and

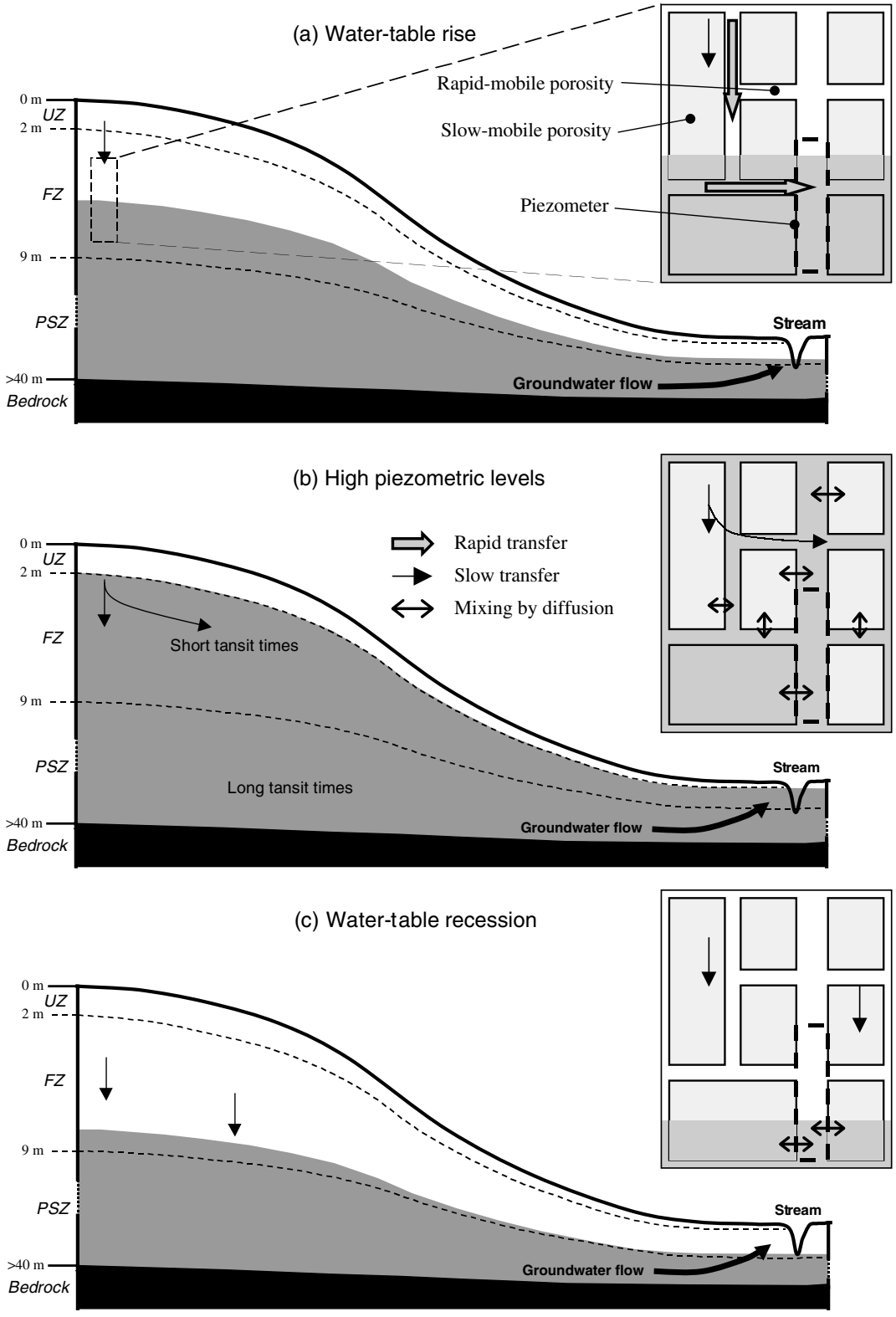

Figure 7 Sketch diagram showing hydrochemical behaviour on a hillslope, with the associated metre-scale mechanisms according to the three periods (a), (b) and (c). A chemical signal is produced in the unsaturated zone (UZ) and transferred through the water-table fluctuation zone (FZ). It migrates either vertically towards the permanently saturated zone (PSZ) or laterally, depending on the water content in the FZ. During period (a), mixing on the metre scale occurs under saturated conditions between the slow-mobile porosity containing solute-rich water and the rapid-mobile porosity containing dilute rainwater.

contributes to saturate the whole bulk volume. It is important to note that a small amount of water can cause a significant rise in the water table, since an analysis of the water-table variations in response to rainfall reveals that the specific yield is around 3% of the bulk volume.

In the early stages of water-table rise, the chloride concentrations at the water table vary from one year to another (Fig. 5) and does not fully reflect the rainfall chloride concentrations, which remain steady at around 10 mg l^{-1} between years. This indicates that the water percolating rapidly may have been in contact with pre-event water from the slow-mobile porosity. The mixing with chloride-rich pre-event water is of variable importance according to the amount and rate at which the chloride-poor rainwater is transferred through the rapid-mobile porosity.

We assume that the chloride concentrations measured from water samples collected in the recently saturated weathered granite are low because the water collected in piezometers can be considered as in continuity with the rapid-mobile porosity compartment (Fig. 7). During water-table rise, the groundwater close to the water table is renewed rapidly since (i) there is a high percolation flux towards the groundwater in response to rainfall (Fig. 2a) and (ii) the groundwater flows rapidly along a horizontal or sub-horizontal direction. This latter point is supported by two lines of evidence. Firstly, the vertical and lateral hydraulic gradients increase as the water table rises, leading to an increase of the groundwater flow. Moreover, the vertical gradient is almost always lower than the lateral gradient. Secondly, some evidence is provided by the geophysical MRS measurements reported by Legchenko et al. (2004). These authors have shown that the water-table fluctuation zone displays higher permeabilities than the permanently saturated zone (3×10^{-6} m s^{-1} at 8 m and 8×10^{-7} m s^{-1} at 15 m). From these two types of evidence, we can conclude that the lateral component of the groundwater flow is more important than the vertical component.

Consequently, during the period of rising water table, the convective flux of solutes in the rapid-mobile porosity is dominant over the diffusive flux of solutes between the slow-mobile and rapid-mobile porosity compartments. Hence, the solute concentrations of the water sampled just below the water table are not affected by diffusion during the early stages following saturation of the medium. Since the groundwater flow follows a sub-horizontal path, there is a gradual increase in contact time between the rapid-mobile porosity and the slow-mobile porosity. Then, diffusion increasingly affects the water chemistry of the rapid-mobile porosity compartment along the groundwater flowpath. This explains why the solute concentrations start to increase in the 8-m and 5-m deep piezometers on around the 19th January 2004 (Fig. 6c), about 20 days before the highest water-table level (Fig. 6b), whereas the concentrations in the 4-m deep piezometer continue to decrease. At that time, the water table is roughly 4 m below the soil surface, and it takes enough time for the dilute water to flow from the water table to these two depths of 5 and 8 m in order to produce an increase in concentrations.

Period (b) — high piezometric level

In contrast to the period of water-table rise, the amount of rainfall decreases as the percolation flux to the groundwater decreases (Figs. 2a and 6b). In the groundwater, the lateral and vertical gradients decrease progressively (Fig. 2c) along with the groundwater flow. As a result, the groundwater is renewed more slowly at the water table. Just below the water table, the solute diffusion fluxes between the two mobile porosity compartments become more and more active compared to the convection flux in the rapid-mobile porosity. Consequently, the solute concentrations increase at all depths (Fig. 6c).

Period (c) — water-table recession

The capillary potentials, and hence the hydraulic heads, decrease progressively in the unsaturated zone, as shown by the hydraulic head profile on the 07th July 2004 in Fig. 6a. The near-surface layer dries out more rapidly during this period due to the increase in the evapotranspiration rate (Fig. 2a). The rapid-mobile porosity desaturates and soon becomes inactive in flow and solute transfer. The only active recharge mechanism is slow piston flow through the slow-mobile porosity compartment. This mechanism supplies chloride-rich water to the groundwater.

Seasonal hydrochemical behaviour at the hillslope scale

As outlined above, a strong chemical variability in groundwater associated with fluctuations of the water table has been observed in regional Chalk aquifers in Northern Europe (Fretwell et al., 2005; Brouyère et al., 2004). In our study, we observed the same kind of variability on a hillslope above shallow groundwater in a headwater catchment. We also show that the classical vertical separation of aquifer profiles into two zones, i.e. unsaturated and saturated, is unsuited to aquifers exhibiting large water-table fluctuations. The water-table fluctuation zone should be considered as a distinct third zone since it has a specific hydrochemical behaviour characterised by mixing between waters of various different origins and age.

The hydrology and biogeochemistry of headwater catchments is currently a matter of debate (Kirchner, 2003; Mc Donnell, 2003; Burt and Pinay, 2005). The debate focuses not only on the stormflow generation processes, but also more generally on the stream flow generation. At present, there is no accepted model for solute transfer along hillslopes from the soil surface to the stream. Given the results presented here, we are able to propose a conceptual model of hillslope hydrochemical behaviour implying variable flowpaths and residence times along the hillslope. We consider three layers (Fig. 7):

1. The unsaturated zone (UZ), extending from the soil surface down to −2 m, is the boundary layer receiving and transferring the rainfall and solutes through different porosity compartments.
2. The zone in which the water table fluctuates — known as the fluctuation zone (FZ) — is completely saturated each year at the end of the water-table rise period, and then

becomes progressively desaturates down to its minimum level at −9 m. This zone is characterised by a great chemical variability with time.
3. The permanently saturated zone (PSZ) is characterised by a steady level of concentrations.

During the water-table rise period (Fig. 7a), rainwater percolates through the slow-mobile porosity of the UZ as long as the rainfall input rate does not exceed the infiltration capacity of the UZ matrix. Once this is reached, rainfall excess is rapidly transferred vertically through the rapid-mobile porosity compartment of the UZ and then the FZ. The solute-poor rainwater represents an input that saturates the bulk volume of the FZ. The low specific yield of the weathered granite can lead to a considerable rise of water-table level. When the FZ is saturated (Fig. 7b), the flow direction changes from vertical — as classically observed in unsaturated conditions — towards sub-horizontal in the recently saturated zone, as shown in our analysis of the water-table rise period. The occurrence of dominant lateral flows at the water-table was also pointed out by Haria and Shand (2004) in a context of a rising water table transferring chemical constituents to the stream channel.

The groundwater flows mainly through the rapid-mobile porosity, or even through the larger pores of the slow-mobile porosity. The solute concentrations of water flowing in this porosity increase progressively along the flowpath from the water table, since the initially solute-poor water interacts with the solute-rich water from the slow-mobile porosity. As a result, during periods where the FZ is saturated, the water reaching the PSZ is highly concentrated.

When the water table decreases, the FZ becomes desaturated. The solute transfer in the FZ is then mainly vertical and slow through the slow-mobile porosity, as seen in the UZ. During the period with the lowest piezometric levels (Fig. 7c), the recharge to the groundwater is low. The FZ behaves in the same way as the UZ during this period. Hence, the PSZ is recharged by solute-rich water flowing vertically through the slow-mobile porosity of the FZ.

In this model, solute molecules present in the FZ exhibit different behaviours according to whether they are located in a zone with partly saturated or completely saturated porosity. In the former case, the solute follows a vertical path with a slow velocity, around 2—3 m per year as recorded in the Kerbernez catchment. In the case of a completely saturated porosity, the solute flowpath in the FZ is more or less lateral. A key point of this conceptual model is that a given solute molecule would successively encounter partially and totally saturated conditions during its path along the hillslope. The solute would move from partially saturated to totally saturated conditions, and inversely, depending on the water-table fluctuation.

Conclusion

We present the results and analysis of a field experiment undertaken to characterise the water chemistry above, at and below the water table of an unconfined groundwater catchment in western France. The observations are analysed to identify the mechanism responsible for solute transfer in the soil—groundwater continuum. The tracer experiments as well as the natural chloride concentrations suggest that two mobile porosity compartments, slow and rapid, are involved in solute transfer within the weathered granite aquifer. In the unsaturated zone of the aquifer, solutes are mainly transferred vertically and slowly at velocities ranging from 2 to 3 m per year through 36—37% of the bulk volume. When the water percolation flux increases, water can percolate rapidly down to the water table through a small fraction of the porosity, equal to 3%. Even though the volume is small, this water can lead to a considerable rise of the water table.

Furthermore, the results show that the water-table fluctuation zone is characterised by a strong temporal variability following a similar pattern from one year to the next. The time scale of the variability is much longer than the rainfall event. This pattern can be explained by considering two mobile porosity compartments and the groundwater hydraulics. During the water-table rise period, the solute-poor rainwater reaching the water table through the rapid-mobile porosity compartment flows laterally below the water table. It is then renewed rapidly by the influx of new solute-poor water through the rapid-mobile porosity, hence limiting mixing with pre-event water from the slow-mobile porosity. During the periods of high piezometric level and water-table recession, the decrease in groundwater flow and percolation water flux from the unsaturated zone leads to a progressive homogenisation of the solute concentrations between the slow-mobile and rapid-mobile porosity compartments. This leads to an increase of solute concentrations in the piezometers in the water-table fluctuation zone.

We discuss here the implications of water-table fluctuations on the solute transfer along a hillslope. From this discussion and the previous observations, we conclude that the water-table fluctuation zone is a mixing zone where water flows more or less laterally in saturated conditions and vertically in unsaturated conditions, depending on the frequency and amplitude of the fluctuations. Mixing in the water fluctuation zone needs to be considered at two spatial scales. Firstly, mixing at the pore scale corresponds to exchanges between the rapid-mobile porosity and the slow-mobile porosity as shown in the discussion. Secondly, mixing at the hillslope scale results from differences of flow path geometry and velocity between unsaturated conditions and saturated conditions. Depending on the frequency and depth of water-table fluctuations, solutes can follow successive vertical and lateral flowpaths. These successive movements can induce a mixing of waters along the hillslope.

Considering the water-table fluctuation zone as a distinct layer in hydrochemical models may result in markedly different estimations of the distribution of solute residence times in headwater catchments compared with the results obtained from stationary models.

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