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Effectiveness of groundwater nitrate removal in a river riparian area: the importance of hydrogeological conditions

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Abstract

Riparian areas are often considered important ecological ecotones that decrease the nitrate load of groundwater discharging into rivers. In this paper, the effectiveness of nitrogen removal from groundwater in a riparian area has been evaluated. We used a quantitative hydrogeological approach which delimited homogeneous stream tubes based on the water table contour. We constructed water and mass balances and used the results to estimate the mass of nitrogen removed by biological processes. Nitrogen removal effectiveness was calculated as the ratio of nitrogen removed to the total nitrogen mass flowing through the riparian area. This approach requires knowledge of the hydrogeological settings and coverage of an area larger than the study site.

The removal we observed was seasonally variable, ranging between 2.2 and 7.6 mg N m^{-2} day^{-1}, and represented up to 95% of the total nitrogen mass entering the riparian area in late summer. Removal effectiveness was only 27–38% in winter, due to the combination of a high nitrogen input and a low plant uptake. Nitrogen removal was highest in spring, but effectiveness was about 60% because the input was as high as in winter. Rainwater infiltrating the riparian area could represent almost the same quantity as groundwater input. Under such conditions, the dilution effect is very important in riparian areas that are not nitrate sources and it is essential to maintain this non-nitrate-emissive use. This study showed that the effectiveness of nitrogen removal in a riparian area is highly dependent on the pathway of water movement through its biologically active layers.

Keywords: Denitrification; Riparian zone; Nitrate removal; Groundwater; Mass balance

1. Introduction

Since much of the nitrate contamination of surface water originates from groundwater recharged in cultivated fields, the nitrate level in groundwater can have a major influence on the quality of surface water (Cey et al., 1999). Riparian areas, defined as three-dimensional zones of direct interaction between terrestrial and aquatic ecosystems (Gregory et al., 1991) constitute the interface between upland and river. Numerous studies have suggested that biological removal (especially denitrification and plant uptake) in riparian areas is an important process that decreases the nitrate load of groundwater discharging into streams (Hill, 1996). Denitrification has been shown to occur within the aquifer on a variety of temporal and special scales (Brüsch and Nilsson, 1993; Pinay et al., 1993; Schnabel et al., 1996; Postma and Boesen, 1991; Smith et al., 1991; Böttcher et al.,

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1990), but its effect on groundwater and surface water nitrate loads has not been well documented (Starr et al., 1996; Böhlke and Denver, 1995). Estimating nitrate retention requires a good knowledge of the hydrogeological settings of the riparian areas under study. These areas could be zones of groundwater upwelling (Nwankwor and Anyaogou, 2000) or downwelling (Cey et al., 1999) or be bypassed at depth by the greatest part of the groundwater flow (Böhlke and Denver, 1995; Burt et al., 1999). Therefore, water flow-paths within riparian areas are often complex and mixing of waters with different nitrate loads could easily be misinterpreted as nitrogen loss. Moreover, riparian areas may have a complex arrangement of different layers, not all of which are biologically active. It is crucial to ascertain what proportion of nitrogen moves through these biologically active layers (Lowrance, 1996) in order to understand the role of a riparian area in removing nitrogen from groundwater. In this paper, we will use the term 'hydrogeological conditions' in its broad sense referring to determining hydrogeological and pedological properties (thickness, hydraulic conductivity, organic matter content) of all aquifer layers in the riparian area, from the bottom of the aquifer to the soil surface.

Riparian areas generally correspond to areas with a permanent cover that is non-cultivated (forest, grassland) or extensively cultivated (meadow, pasture). These areas are not nitrate sources compared to adjacent agricultural lands and there is no significant nitrate load in the rainwater infiltrating these areas. Rainfall infiltration induces a dilution effect that must be distinguished from biological removal. Therefore, characterising all the different water flows, as well as the nitrogen content of each component of such complex systems, constitutes an essential step in quantifying the effectiveness of nitrate removal compared to total groundwater discharge into the river.

This study focuses on groundwater nitrate depletion within a forested riparian area. The objectives are: (i) to calculate and discuss the effectiveness of a riparian area while distinguishing the dilution effect of rainwater infiltration from biological nitrogen removal and (ii) to show the role of hydrogeological conditions in the control of loads of nitrogen flowing through riparian areas.

2. Materials and methods

2.1. Study site

The study site is located at the foot of the Jura mountains in Switzerland and belongs to the geographical unit of the Swiss Plateau (46°36′N; 6°24′E). Site elevation is about 660 m (msl) with mean annual precipitation of 1280 mm (1961–1990, Swiss meteorological institute data). It borders the Morand River which has an average winter discharge of 3 m^3/min. The site is a forested riparian area (dominant tree species include *Alnus glutinosa*, *Fraxinus excelsior* and *Prunus padus*), and is adjacent to an extensive long-duration meadow (Fig. 1).

Geologically the site consists of recent glacial deposits (Würm). The geological structure was understood from lithological descriptions (Fig. 2). The valley is U-shaped, formed on a till (compacted silty-clayed formation) and filled with fluvioglacial material (sandy gravels to sands). Some silt lenses occur at the bottom or top of the fluvioglacial formation. The thickness of the fluvioglacial formation varies from 5 m (middle of the meadow) to 20 cm (near the river). This fluvioglacial formation contains a regional groundwater flow used for water supply. Its outlet generates a wetland that is the spring of the Morand river. The catchment of this regional flow is about 0.06 km^2 in size. It is characterised by a crop-livestock farming system, the part of grassland being about 50% while main annual crop is winter wheat. This agricultural use produces moderate levels of nitrate and chloride in the groundwater (about 6 mg N l^{-1} and 14 mg Cl l^{-1}—average of six well supplies sampled between 1998 and 2000). The study site is part of this wetland and edges the Morand river. Downstream, the till constitutes the banks of the Morand river and geological conditions cause a thin lateral sub-surface flow directly on this low-conductivity substratum towards the river. The soil of the study site, described in detail in Cosandey et al. (2003a) is a non-evoluted, organic soil (Terric Histosol in the FAO classification) developed directly from the fluvioglacial gravels. The organic horizon varies in thickness (30–120 cm). Locally, we observed an organomineral transition horizon (that we classified with the organic horizon). Organic carbon content was calculated from the difference between the total carbon content (measured

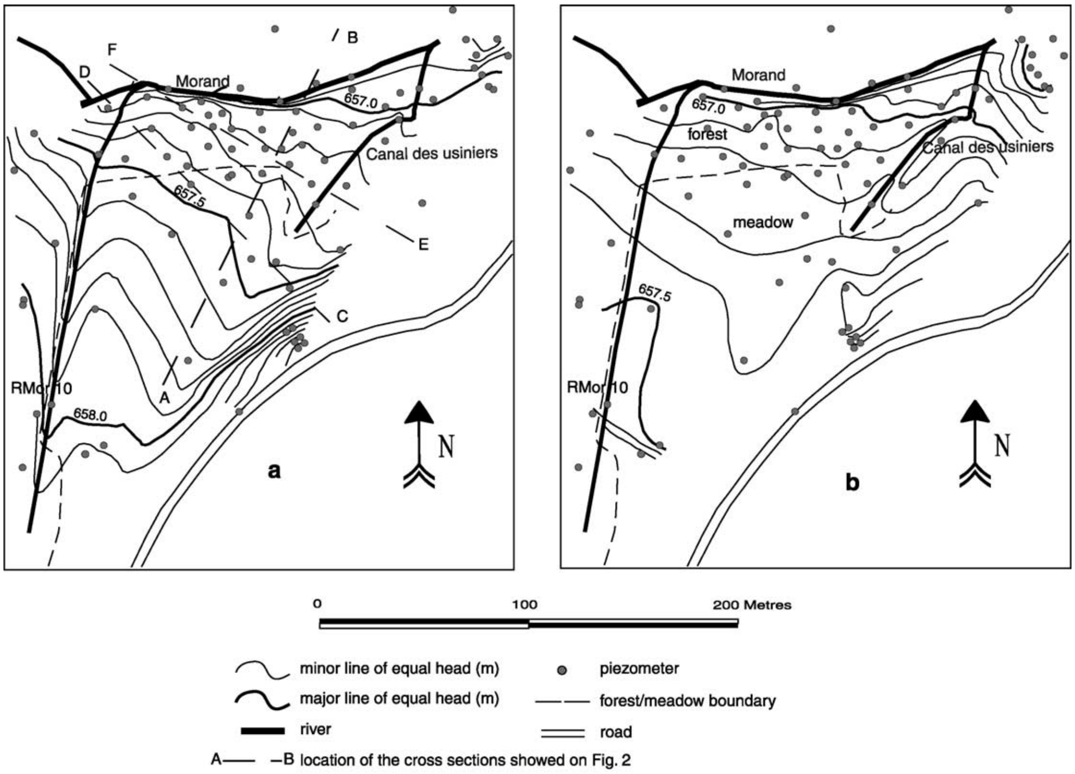

Fig. 1. Piezometric network and a—location of the cross-sections given in Fig. 2, piezometric map drawn for the high-water period; b—forest/meadow boundary, piezometric map drawn for the low-water period.

by means of 1000 °C combustion under oxygen flow using a carbon analyser) and the mineral carbon content (measured using the same analyser after dilution in phosphoric acid). It is much greater both for the organic horizon (12.2%) and the transition horizon (8.7%) than for the fluvioglacial formation (0.8%). Hydraulic conductivity ranges between 7.10^{-6} and 7.10^{-4} m s^{-1}. The higher hydraulic conductivities correspond both to the fluvioglacial formation and the organic layer. In the western part of the site, only the organic horizon represents the aquifer formation. The lower hydraulic conductivities correspond to the till that constitutes an aquitard with respect to the groundwater flow.

2.2. Hydrogeological investigations

A set of piezometers was installed in an area larger than the riparian area to understand its three-dimensional water dynamics and the relationship between river water and groundwater (Fig. 1). The piezometers were PVC pipes (8 cm id) installed in holes drilled by hand auger. Pellets of bentonite were poured around the top of the piezometers to impede direct infiltration of rain along the tube. Most piezometers were perforated throughout their length, except the first 20 cm below the soil surface. Some were perforated only at the bottom to examine the stratification of piezometric and chemical properties in our site. In these cases, a bentonite seal was installed to isolate the tested section of the aquifer.

Saturated hydraulic conductivities were measured by pumping tests in piezometers. They were calculated using the Jacob formula defined in Freeze and Cherry (1979), the Lefranc formula defined in Mabillot (1995) or the Babouchkine and Guirinsky formula defined in Castany (1967), depending on the local characteristics of the tested piezometers.

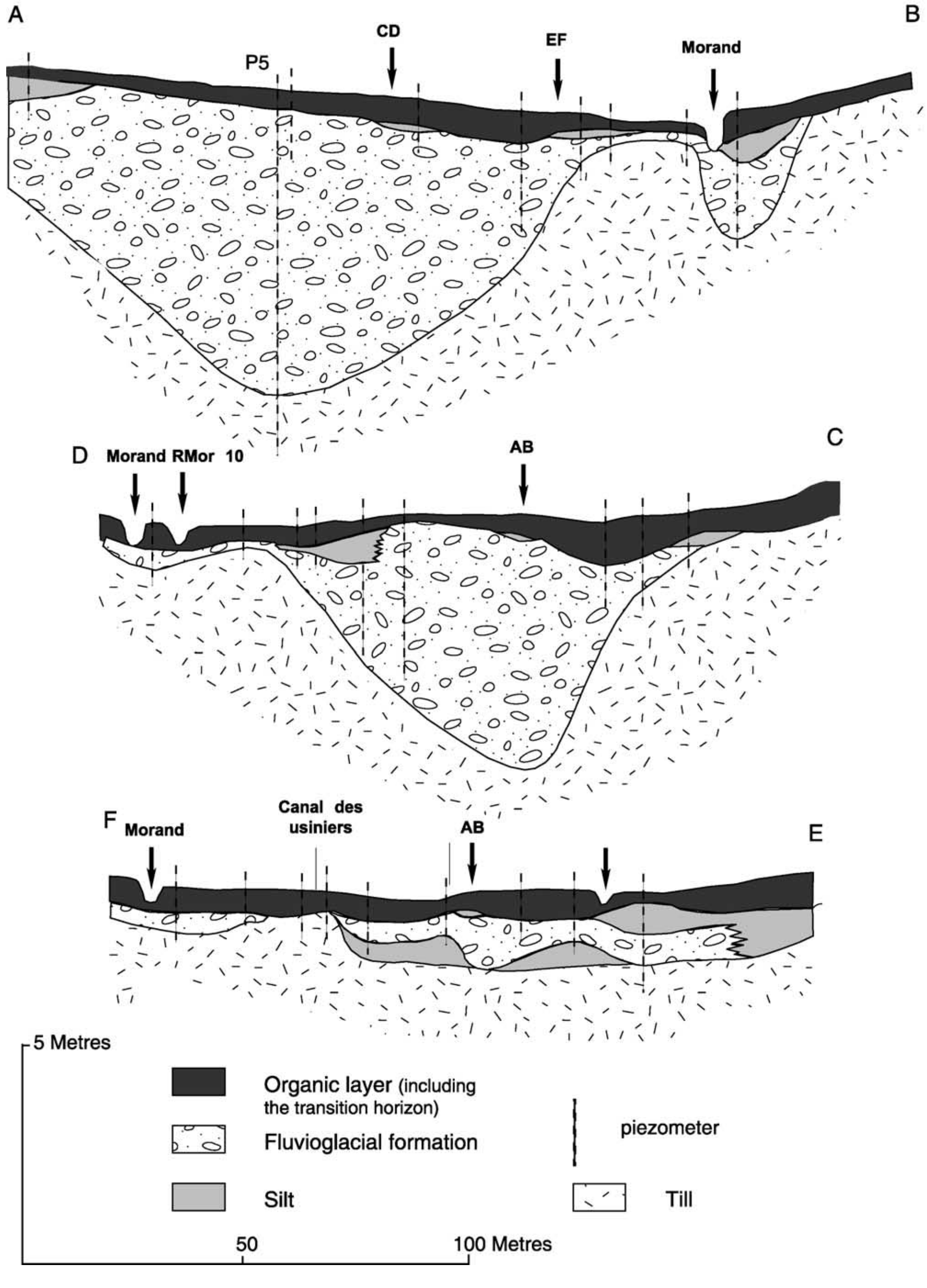

Fig. 2. Geological structure of the studied site (the cross-sections are indicated in Fig. 1).

Lithology (presence of organic matter, granulometric estimation and thickness) was determined by visual inspection of cores collected by hand auger during installation. A bore hole (P5 in Fig. 2) was drilled to the till where the aquifer is deepest. Water levels were measured monthly from January 1999 to July 2000 and contour maps of the water table were drawn by hand for each date of measurement.

2.3. Water chemistry

Once the water level had been measured, at least one volume of the piezometer content was removed. The groundwater was then sampled manually. The water was filtered in the field, immediately after sampling, with a syringe-adaptable system using fibreglass pre-ashed 0.2 μm filters (Whatman™ ref. GF/F); the samples were stored at 4 °C until analysis. Nitrite and ammonium contents were analysed using the colorimetric methods (sulphanilamide *N*-1-naphthylethylenediamine and indophenol blue method (Stainton et al., 1977), respectively). Nitrate and chloride were measured by ion chromatography (Dionex DX3500). Nitrate and chloride were analysed monthly from January 1999 to July 2000, whereas ammonium and nitrite were measured only until January 2000.

2.4. Methodology for flux calculation

To construct balances of water, chloride and nitrogen, we used the stream tube concept (Kresic, 1997). These stream tubes are three-dimensional bodies determined from the contour map of the water table. Their lateral boundaries correspond to vertical stream surfaces and their upslope (referring to the groundwater movement through the stream tube) and downslope boundaries correspond to equipotential surfaces that are assumed to be vertical. Therefore, this contour depends on the shape of the contour map and must be adapted for each date of water and nutrient samples. There is no gain or loss of water in the portion of the aquifer bound by two stream surfaces. Therefore, inside a stream tube, exchanges are possible only from the bottom and top boundaries. In our site, the bottom boundary corresponds to the impermeable till, where no exchange is possible. Exchanges at the top boundary correspond to rain/evapotranspiration effects. These stream tubes are referred to as zones in this paper.

Each zone is characterised by an input section and an output section; both are vertical and made up of different layers, depending on the lithology. The groundwater flows were calculated using the Darcy law for both sections, while taking into account the hydraulic conductivity and vertical area of each layer. The area of each layer was estimated from the geological structure of the aquifer formation. For each date, the hydraulic gradient was calculated, from the contour map of the water table, for both input and output sections.

The balances were constructed as follows:

- The groundwater flow was calculated for each layer of the input section and for each layer of the output section

$$Q_i = K_i A_i \frac{\Delta h}{l} \tag{1}$$

  Q_i = groundwater flow in layer i
  K_i = hydraulic conductivity of layer i
  A_i = vertical area of layer i
  $\Delta h/l$ = local hydraulic gradient (Δh = hydraulic head difference between two adjacent equipotential lines, l = spacing between two adjacent equipotential lines).

- The groundwater flow (Q) for a section was calculated as the sum of the groundwater flows of each layer of the section. This was done in the same way for both the input and output sections, i.e. (example is given for calculation of groundwater flow in the input section):

$$Q_{\text{groundwater input}} = \sum_{i=1}^{n} Q_i = \sum_{i=1}^{n} (K_i A_i) \frac{\Delta h}{l} \tag{2}$$

  where n is the number of layers constituting the input section.

Thus, the groundwater flow calculated for the input section corresponds to the groundwater input to the zone, and the groundwater flow calculated for the output section corresponds to the groundwater output from the zone.

- The top boundary corresponds to the exchanges with the surface, estimated from effective precipitation ($P - \text{PET}$), averaged for a period of 75 days before the calculation date. The values correspond to the daily data of the Swiss meteorological institute and are defined as follows:

$$Q_{\text{top-boundary}} = P - \text{PET} \tag{3}$$

  P = daily precipitation

PET = daily evapotranspiration calculated from the Swiss formula of Primault (1962, 1981).

The value ($P-$ PET) can be positive or negative. Positive values represent rainwater infiltration and correspond to an input. Thus, in our case, where there is no bottom boundary exchange, total input corresponds to the sum of groundwater input plus the value ($P-$ PET). Negative values correspond to an output. Thus, the total output corresponds to the sum of groundwater output plus the value ($P-$ PET).

- From the water flow calculation, we determined the mass of a conservative element. Chloride was used as a conservative element, since the geological layers contained no chloride. The equation used is (for example, the amount of chloride arriving into the input section $F_{Cl^- \text{input}}$) :

$$F_{Cl^- \text{input}} = \sum_{i=1}^{n} Q_i[Cl^-]_i \tag{4}$$

n = number of layers making up the input section
Q_i = groundwater flow in layer i
$[Cl^-]_i$ = chloride concentration in the groundwater flowing into layer i.

Chloride concentrations measured in groundwater sampled from piezometers were assumed to represent an entire layer (see details below). When several piezometers had been chosen as being representative, the amounts of chloride were calculated using the average concentrations of these different representative piezometers. The chloride concentration in infiltrating rainwater was measured in superficial piezometers installed in an area of the meadow hydrodynamically isolated from agricultural loads.

- The water balance and chloride balance were calculated as follows:

$$\text{Water balance} = Q_{\text{input}} + Q_{\text{top-boundary}} - Q_{\text{output}} \tag{5}$$

$$\text{Chloride balance} = F_{Cl^- \text{input}} + F_{Cl^- \text{top-boundary}} - F_{Cl^- \text{output}} \tag{6}$$

For both the water and chloride balances, we accepted the system as well-balanced when the values (water balance/Q_{input}) and (chloride balance/$F_{Cl^- \text{output}}$) were less than 10%.

- We calculated the nitrogen balance using the same method. Since the chloride balance already accounts for all the mixing-dilution effects as well as for dispersion–diffusion effects, the difference corresponds to processes that removed nitrogen mass (Altman and Parizek, 1995; Nelson et al., 1995). These processes may include denitrification, net assimilation by plants or net immobilisation by bacteria (Hill, 1996); they correspond to a biological removal, which does not affect the chloride balance. This method allows us to quantify the net biological removal of the riparian area

$$\text{N balance} = F_{\text{N removed}} \tag{7}$$

N corresponds to the total dissolved inorganic nitrogen (abbreviated to DIN in the text) contained in groundwater.

The effectiveness of the studied zone was calculated by a comparison between the value of the removed DIN and the value of the DIN input.

$$\text{Effectiveness of the biological removal}(\%) = (F_{\text{N removed}}/F_{\text{N input}})100 \tag{8}$$

- The effect of the rain (referred to as rain dilution in the text) was estimated in the same way, when the value ($P-$ PET) was positive:

$$\text{Rain dilution effect}(\%) = (Q_{\text{top-boundary}}/Q_{\text{input}})100. \tag{9}$$

3. Results

3.1. Hydrogeological conditions

Hydraulic conditions. The hydraulic gradient (Fig. 1) shows that the groundwater flow is located in the fluvioglacial formation. Its direction is about N45°E, during both 'high water' and 'low water' situations. During the 'high water' period, the general gradient is about 5‰ and increases near the Morand River. During the low water period, the gradient decreases to values of about 1.5‰ and the groundwater flow is limited to the U-shaped structure. The high water period extends from November to July. The low water period is short, lasting from only July to October. The Morand River drains groundwater flow throughout the year, even during the low water period.

Delimitation of zones. Two zones (east zone and west zone) were delimited in the riparian forest according to the piezometric map (Fig. 3, example given for April 1999). They can be considered as isolated hydrogeological systems. A schematic cross-section of the stream tubes is given in Fig. 4 for April 1999. Piezometers representative of the input and ouput sections (Table 1) have been selected according to the depth of the perforated zone as well as the quality of equipment. The perforated zone is indicated in Fig. 4. In both zones, the aquifer thickness decreases towards the river. In the west zone, the aquifer thickness diminishes from 140 to about 50 cm, whereas the organic layer's thickness does not change; thus, the proportion of the organic part increases in the aquifer. For this zone, the piezometers were assumed to represent the entire aquifer. The aquifer thickness in the input section is greater in the east zone than in the west zone, attaining 3.5 m, about one third of which is an organic layer. Near the river, the aquifer thickness varies between 0.4 and 0.6 m and is mainly organic. For the input section of the east zone, the superficial piezometers represent the shallow part of the aquifer and sample the water flowing through the organic layer. The deep piezometers sample the water flowing through the mineral fluvioglacial formation.

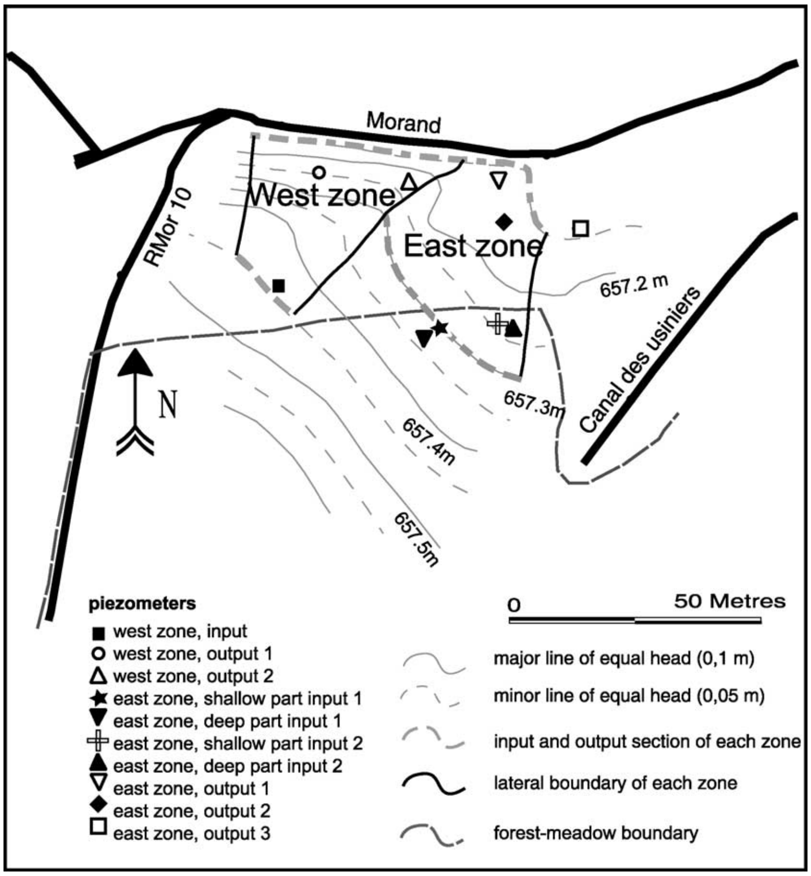

Fig. 3. Delimitation of the two zones according to the contour map of the water table—example given for April 1999.

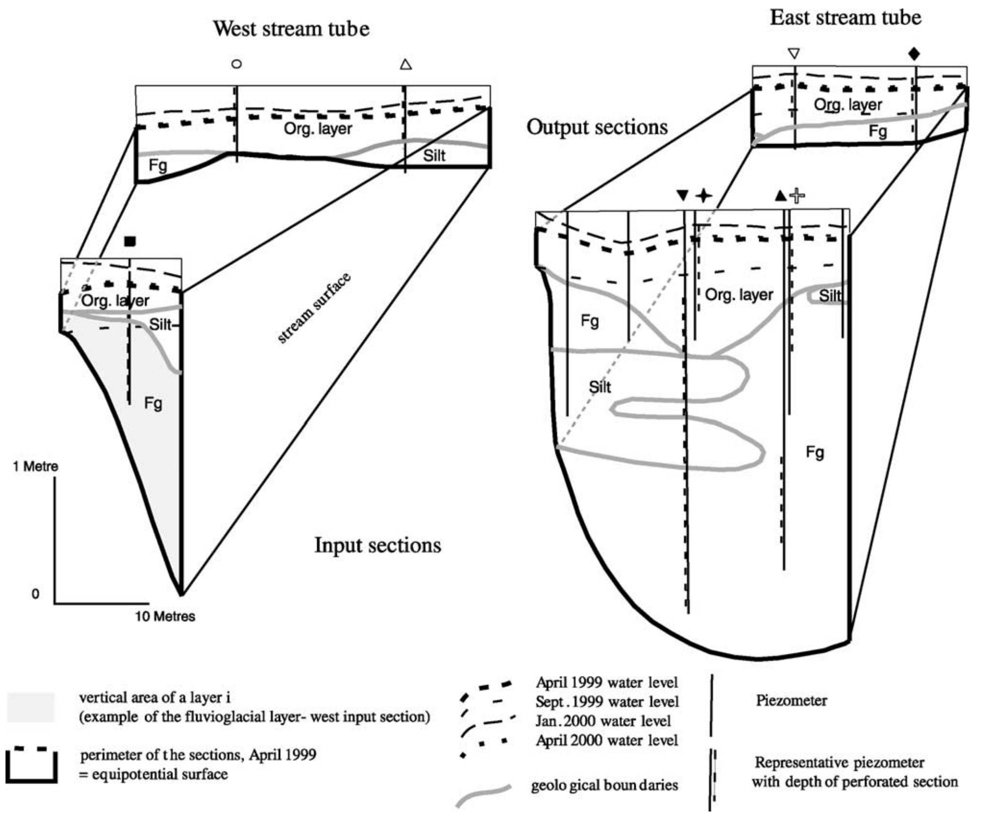

Fig. 4. Schematic cross-section of the two stream tubes (lateral boundaries correspond to conditions prevailing in April 1999).

Table 1
Thickness of fluvioglacial formation and organic layers for the chosen representative piezometers in the two zones

		Representative piezometers	Fluvioglacial formation thickness[a] (m)	Organic layer thickness[a] (m)
West zone	Input 1	Total groundwater thickness	0.95	0.45
	Output 1	Total groundwater thickness	0.20	0.30
	Output 2	Total groundwater thickness	0	0.40
East zone	Input, shallow part 1	Shallow part of the groundwater	2.4	1.10
	Input, shallow part 2	Shallow part of the groundwater	2.7	0.80
	Input, deep part 1	Deep part of the groundwater	2.4	1.10
	Input, deep part 2	Deep part of the groundwater	2.7	0.80
	Output 1	Total groundwater thickness	0.15	0.45
	Output 2	Total groundwater thickness	0.20	0.40
	Output 3	Total groundwater thickness	0.20	0.20

[a] The combine depth of the fluvioglacial formation and organic layers corresponds to the aquifer thickness.

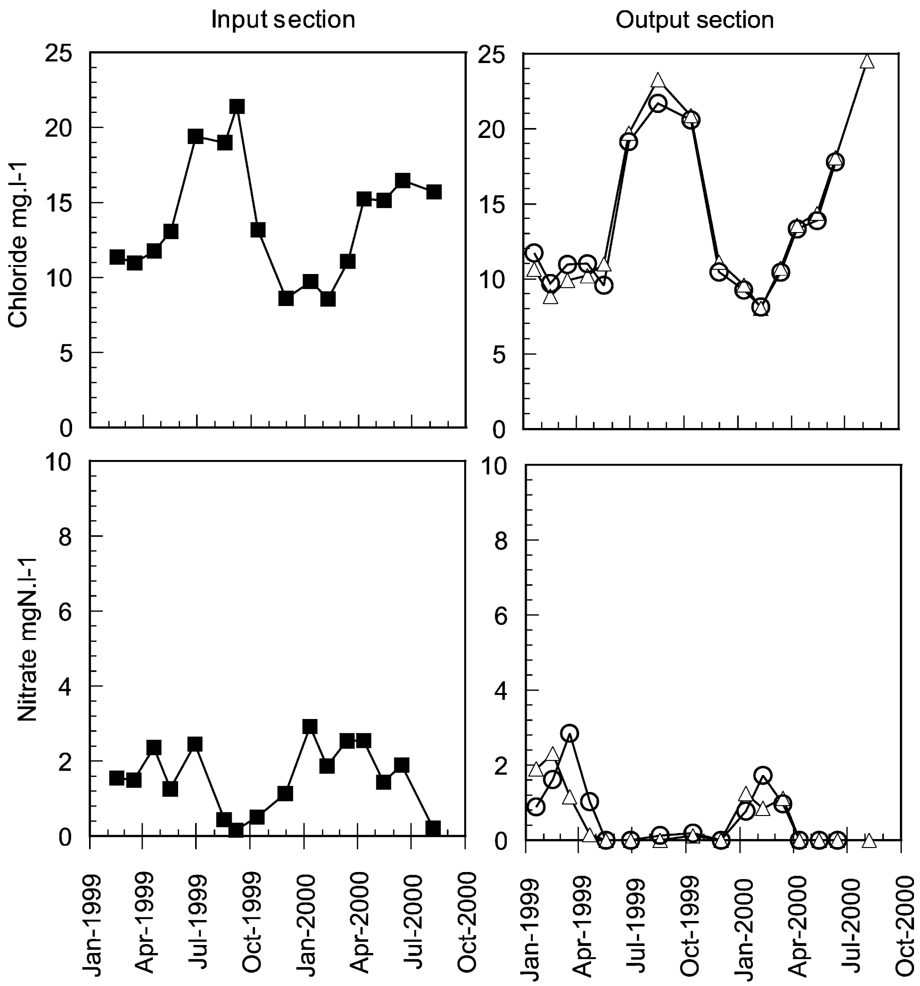

Fig. 5. Time evolution of nitrate and chloride concentrations in the representative piezometers of the west zone. ■ Input groundwater; ○ output groundwater 1; △ output groundwater 2.

3.2. Dynamics of nitrate concentrations

The temporal variation of nitrate and chloride concentrations in the selected piezometers was examined. In the west zone (Fig. 5), we observed a clear seasonal trend. Nitrate concentrations in groundwater were highest in winter (1–2 mg N l^{-1}) and decreased in summer in the input section and in spring in the output section. Then, they remained very low (undetectable values, i.e. less than 0.1 mg N l^{-1}) until they increased again at the beginning of the following winter to levels equivalent to the previous winter. The observed chloride concentrations showed a reverse dynamic; the values were at their minimum in winter and increased rapidly at the beginning of summer to reach their maximum in August/September, quickly decreasing at the beginning of autumn.

In the east zone (Fig. 6), nitrate concentrations in the shallow part of groundwater entering the riparian zone, as well as in groundwater near the river, followed the same temporal pattern as that observed in the west zone. Chloride dynamics were the reverse of nitrate dynamics, as observed in the west zone. In contrast, nitrate concentrations as well of chloride

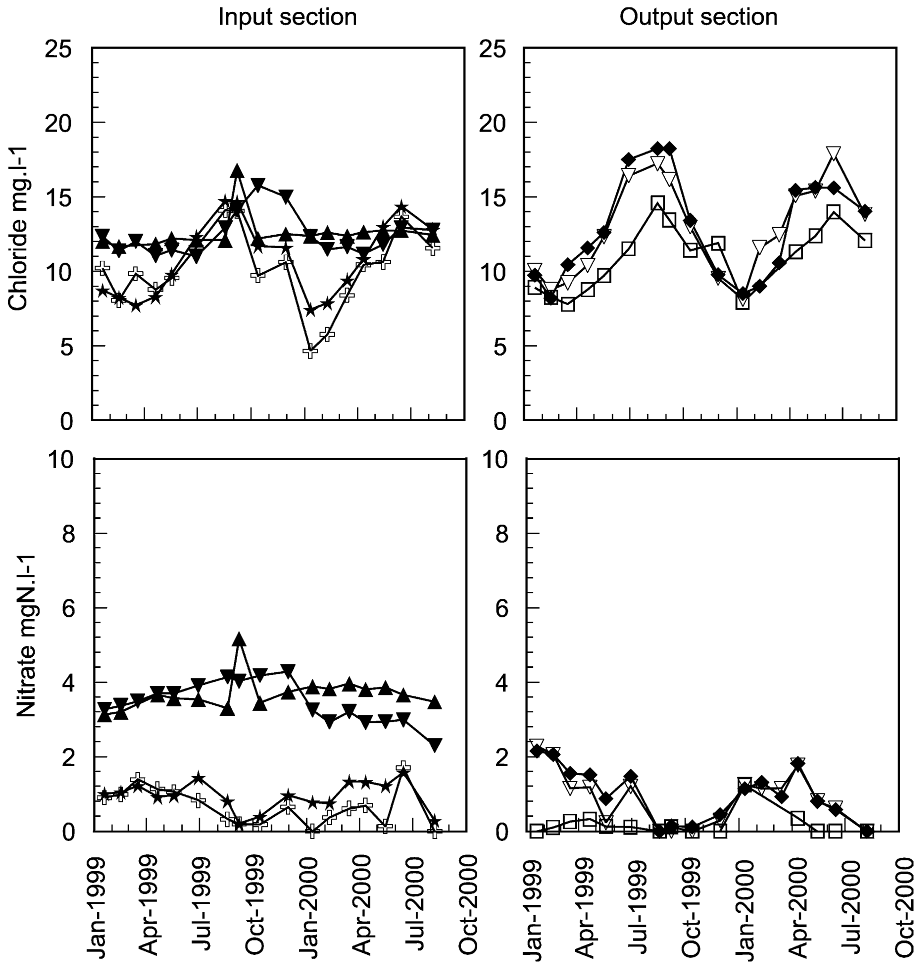

Fig. 6. Time evolution of nitrate and chloride concentrations in the representative piezometers of the east zone. ✦ Input groundwater shallow part 1; ✣ input groundwater shallow part 2; ▼ input groundwater deep part 1; ▲ input groundwater deep part 2; ▽ output groundwater 1; ◆ output groundwater 2; □ output groundwater 3.

concentrations, were higher in the deep part of groundwater entering the riparian zone than its shallow part (about 3–4 mg N l^{-1}) and remained constant throughout the observation period. The studied area corresponding to the outlet of a regional groundwater flow, located in the fluvioglacial formation, these high nitrate and high chloride inputs into the riparian zone are the result of the intensive agricultural use of the watershed.

Based on the combination of the different seasons with the nitrate dynamics, three dates (April 1999, September 1999 and January 2000) were chosen for calculation of nitrogen-removal effectiveness. April 1999 and January 2000 showed the highest nitrate concentrations. The first date represents the biologically active season of early spring, while the second corresponds to the biologically dormant season of winter. Both dates fall during the high water period. On the contrary, September 1999 showed very low nitrate concentrations. This date is in the biologically active season (early autumn) during the low water period.

3.3. Effectiveness calculation

Different forms of nitrogen in groundwater. DIN concentrations of each representative piezometer are

Table 2
DIN concentrations (mg N l^{-1}) for the three typical dates in each piezometer—values in parentheses indicate ammonium percentage

		April 1999	September 1999	January 2000
West zone	Input 1	2.46 (4)	0.62 (74)	2.92 (0)
	Output 1	1.03 (0)	No water	0.78 (0)
	Output 2	0.15 (0)	No water	1.37 (9)
East zone	Input, shallow part 1	0.92 (0)	0.36 (44)	0.78 (0)
	Input, shallow part 2	1.13 (0)	0.19 (0)	0.22 (100)
	Input, deep part 1	3.70 (0)	4.03 (0)	3.25 (0)
	Input, deep part 2	3.66 (0)	5.57 (7)	3.88 (0)
	Output 1	1.18 (0)	0.15 (100)	1.39 (10)
	Output 2	1.51 (0)	0.29 (52)	1.14 (0)
	Output 3	0.32 (0)	0.29 (59)	1.24 (0)

Nitrite concentrations were always less than 0.05, often less than 0.01 mg N l^{-1} and are considered negligible.

given in Table 2 for these three dates. Nitrite concentrations were measured in all samples and were always less than 0.05 mg N l^{-1}, and often less than 0.01 mg N l^{-1}, which was thus considered negligible. Ammonium concentrations were undetectable (<0.03 mg N l^{-1}) in most groundwater during the high water period, i.e. April 1999 and January 2000. In contrast, most groundwater sampled during the low water period contained ammonium (from 0.15 to 0.46 mg N l^{-1}). Moreover, except for the deep part of the groundwater in the east zone, ammonium concentrations represented an important part of the DIN during this low water period (from 44 to 100%).

Construction of mass balances. Detailed calculations of the balances for water, chloride and DIN in the two zones are provided in Table 3 for April 1999 and summarised for all three dates in Table 4. In both the west and east zones, the proportions (water balance/Q_{input}) were, respectively, -6 and -3% for April 1999, and -10 and $+6\%$ for January 2000. The proportion was $+7\%$ for the east zone, whereas the west zone was dry in September 1999. For the chloride balances, the proportions (chloride balance/$F_{\text{Cl}^{-}\text{input}}$) were, respectively, $+9$ and $+7\%$ for April 1999, $+10$ and $+8\%$ for January 2000 and -10% for September 1999.

Rain dilution effect. For April 1999 and January 2000, the values ($P-\text{PET}$) were positive, respectively, 1.1 and 2.2 mm per day. In September 1999, the value was negative, $-$ 0.2 mm per day. Rainwater infiltrating the two zones corresponds to the groundwater recharge as it flows through each. For each zone, comparison of infiltrated rainwater quantity to the groundwater input emphasises the importance of rainfall. Indeed, in April 1999, infiltrated rain represented half the groundwater flow entering the west zone and a third of groundwater flow entering the east zone. In January 2000, the infiltrated rain flow represented almost the same quantity as the groundwater input to the two zones. In contrast, the evapotranspiration process dried up the west zone in September 1999. The chloride concentration dynamics reflects this rain/evapotranspiration effect both in the shallow part of the thick groundwater and the total thickness of thinner groundwater.

Biological removal in the forested riparian area. As the two zones can be considered isolated hydrogeological systems, the value of the DIN balance corresponds to the DIN removal by biological processes. The value of the removed DIN and that of the proportion of removed DIN compared to the DIN input were calculated for the three typical dates (Table 4). The biological removal was also reported by unit of soil surface, to facilitate comparison with previous literature. Finally, the proportion of the groundwater flow passing through the organic layer was calculated for the two zones and for the three dates (Table 5).

For the three dates, both zones act as a net sink for nitrogen. In winter, the quantity of DIN removed is equivalent for the two zones (2.2 mg N m^{-2} day^{-1} east zone, 2.8 mg N m^{-2} day^{-} west zone). During this period, DIN inputs are high in both zones. The biological effectiveness was low, 27% in the east zone

Table 3
Water, chloride and nitrogen balances for the two zones, example given for April 1999

		$P-\text{PET}$ (mm day^{-1})	Hydraulic conductivity, K (m s^{-1})	Hydraulic gradient (‰)	Area (m^{-2})	Groundwater flow (m^3 s^{-1})	Chloride concentration (mg l^{-1})	DIN concentration (mg N l^{-1})	Chloride mass (g s^{-1})	DIN mass (g N s^{-1})
East zone										
Input section	Organic horizon		2.5×10^{-5}	6	21.4	3.21×10^{-6}	8.5	1	2.73×10^{-5}	3.21×10^{-6}
	Silt		1.0×10^{-6}	6	18.6	1.12×10^{-7}	11.4	3.7	1.27×10^{-6}	4.13×10^{-7}
	Fluvioglacial gravels		8.5×10^{-5}	6	70.5	3.60×10^{-5}	11.4	3.7	4.10×10^{-4}	1.33×10^{-4}
	Groundwater input (sum)					3.93×10^{-5}			4.38×10^{-4}	1.37×10^{-4}
Output section	Organic horizon		2.5×10^{-4}	14.7	6.8	2.50×10^{-5}	10.2	1	2.55×10^{-4}	2.50×10^{-5}
	Silt		1.0×10^{-6}	14.7	0	0	10.2	1	0	0
	Fluvioglacial gravels		3.7×10^{-4}	14.7	4.8	2.61×10^{-5}	10.2	1	2.66×10^{-4}	2.61×10^{-5}
	Groundwater input (sum)					5.11×10^{-5}			5.21×10^{-4}	5.11×10^{-5}
Top boundary		1.13			990.0	1.29×10^{-5}	4	0.15	5.18×10^{-5}	1.94×10^{-6}
Bottom boundary						0			0	0
Balance						-1.13×10^{-6}			3.10×10^{-5}	-8.75×10^{-5}
Balance/input (%)						-3			$+7$	
West zone										
Input section	Organic horizon		3.0×10^{-4}	4.9	2.8	4.12×10^{-6}	12	2.5	4.94×10^{-5}	1.03×10^{-5}
	Silt		1.0×10^{-6}	4.9	2.1	1.03×10^{-8}	12	2.5	1.23×10^{-7}	2.57×10^{-8}
	Fluvioglacial gravels		2.8×10^{-4}	4.9	13.3	1.79×10^{-5}	12	2.5	2.15×10^{-4}	4.48×10^{-5}
	Groundwater input (sum)					2.20×10^{-5}			2.65×10^{-4}	5.51×10^{-5}
Output section	Organic horizon		7.0×10^{-5}	35	11.1	1.12×10^{-7}	10.5	0.6	2.86×10^{-4}	1.63×10^{-5}
	Silt		1.0×10^{-6}	35	3.2	4.20×10^{-6}	10.5	0.6	1.18×10^{-6}	6.72×10^{-8}
	Fluvioglacial gravels		8.0×10^{-5}	35	1.5		10.5	0.6	4.41×10^{-5}	2.52×10^{-6}
	Groundwater input (sum)					3.15×10^{-5}			3.31×10^{-4}	1.89×10^{-5}
Top boundary		1.13			832.7	1.09×10^{-5}	4	0.15	4.36×10^{-5}	1.63×10^{-6}
Bottom boundary						0			0	0
Balance						-1.43×10^{-6}			2.27×10^{-5}	-3.78×10^{-5}
Balance/input (%)						-6			$+9$	

Table 4
Main calculated values for the three typical dates, in the two zones

	Q_{input} (m^3 day^{-1})	$Q_{top\text{-}boundary}$ (m^3 day^{-1})	Water balance/ Q_{input} (%)	Chloride balance/ F_{Cl^-} input (%)	Rain dilution effect (%)	$F_{N\ input}$ (gN day^{-1})	DIN removal (gN day^{-1})	Effectiveness of removal (%)	DIN removal/ area[b] (mgN m^{-2} day^{-1})
April 1999									
East zone	3.4	1.11	−3	+7	33	11.8	7.6	64	7.6
West zone	1.9	0.94	−6	+9	49	4.8	3.3	69	3.9
September 1999									
East zone	1.05	−0.21	7	−10	No dilution	4.8	4.6	95	4.3
West zone			Output section is dry						
January 2000									
East zone	2.62	2.39	+6	+8	91	8.6	2.3	27	2.2
West zone	2.46	2.20	−10	+10	90	7.2	2.7	38	2.8

[a] Area corresponds to the soil area above the top-boundary of the stream tube (vertical projection).

and 38% in the west zone. In spring, the removal calculated for the east zone was 7.6 mg N m^{-2} day^{-1}; this is almost twice the calculated value for the west zone (3.9 mg N m^{-2} day^{-1}). The biological effectiveness is high, representing more than 60% of the DIN inputs in the two zones. In autumn, calculated DIN removal is intermediate (4.3 mg N m^{-2} day^{-1}) in the east zone, whereas the west zone is dry. The value for the east zone represents a biological effectiveness of 95%. Although mass removal is lower in September than in January and April, the effectiveness is high because DIN inputs are lower. For each date, the effectiveness is higher in the west zone than in the east zone because DIN inputs are lower in the former. Indeed, not only is the aquifer thicker and more water is entering the east zone than the west, but DIN concentrations are also higher in the water entering the east zone, especially during spring/summer.

4. Discussion

4.1. Effectiveness of nitrogen removal in the two zones

Total dissolved inorganic nitrogen. Processes resulting in nitrate transformation into another inorganic form may include microbial ammonification, mineralisation of organic nitrogen and ammonium exchange to sediments. Especially in such organic and saturated environments, very

Table 5
Proportion of groundwater flowing through the organic horizons for the three dates, in the two zones

	Total input groundwater flow (m^3 day^{-1})	Input groundwater flow passing through the organic horizons (%)	Total output groundwater flow (m^3 day^{-1})	Output groundwater flow passing through the organic horizons (%)
April 1999				
East zone	3.4	8.2	4.42	48.9
West zone	1.9	18.7	2.72	86.3
September 1999				
East zone	1.05	4.7	0.92	7.2
West zone	dry			
January 2000				
East zone	2.62	9.1	5.16	51.9
West zone	2.46	34.3	4.42	80.8

reducing conditions may prevail, at least locally and temporarily. Dissimilatory nitrate reduction could occur and transform nitrate forms into ammonium in the presence of bacterial organisms (Howard, 1985; Tiedje, 1988; Tiedje et al., 1981); this process has been demonstrated to occur in cultures of bacteria (Rehr and Klemme, 1989; Fazzolari et al., 1990). It is important not to ignore ammonium production, because permissible level for ammonium in drinking water is much lower than for nitrate (WHO, 1996). Since we cannot neglect these processes in our study site, and because ammonium content is not negligible in some of our groundwater, especially during the low water period (Table 2), we chose to construct mass balances for total dissolved inorganic nitrogen. Actually, the aim of this work is to quantify the net nitrogen removal by biological processes in the studied riparian area, not to quantify each of the processes.

Rain dilution effect. Rainwater infiltration has a very significant effect since rain recharge represents as much as 90% of the groundwater flow entering both zones in winter (Table 4). As the DIN content in infiltrating rain water is very low compared to the groundwater DIN content, rain dilution affects strongly the groundwater DIN output too. As a matter of fact, in our site, all conditions (moderate groundwater flow, high precipitation in winter, wide non-cropped riparian areas) are met for rain dilution effect to be significant. These conditions are frequently combined in this geographical unit. Our calculated groundwater flow (about 0.09 m^3 day^{-1}) has the same magnitude as the sub-surface flow on the till, upstream the study site (Cosandey et al., 2001—0.07 m^3 day^{-1}). Such a seasonal pattern was observed by several authors (Lowrance et al., 1984; Brüsch and Nilsson, 1993), but the dilution effect was not quantified. Cey et al. (1999) and Devito et al. (2000) already showed that nitrogen concentrations in shallow groundwater discharging into a river may result from areas with less intensive farming. Since rain infiltration could be of the same magnitude as groundwater flow, it is essential not to create additional nitrogen loads in rainwater infiltrating riparian areas and discharging into groundwater. This factor makes it even more necessary to maintain a non-cropped use (forest, grassland), i.e. a non-nitrate-emissive use, in riparian areas when managing landscape.

Biological removal. Assessment of the proportion of water passing through the organic horizon provides a better understanding of patterns of nitrate removal in the riparian zone. In the studied area, groundwater is forced to flow through the superficial layers due to the geological structure. The aquifer thickness decreases from 1.4 to 3.5 m near the meadow riparian boundary to only 0.4–0.6 m near the river. These specific conditions improve the chances for biological processes (denitrification, plant uptake, reductive dissimilation) to affect nitrogen contained in groundwater. The superficial layers consist of the organic horizon and the organomineral transition horizon; both represent the microbiologically active layer and contain most of the roots. On our site, Cosandey et al. (2003a) measured the denitrifying enzyme assay (DEA), adding excess of nitrate and carbon (Smith and Tiedje, 1979). The organic horizons showed a DEA activity 100 times higher (14.6 mg N per unit of soil weight (g) per day) than the mineral horizons (0.15 mg N per unit of soil weight (g) per day). Thus there is evidence of a lack of denitrifying bacterial population in our mineral aquifer horizon and maximal activity occurs in surface horizons. Similar results were found in other studies. Burt et al. (1999), for example, showed that little denitrification activity occurred below 40 cm and concluded that there was no evidence of significant deep denitrification. In addition, fluvioglacial gravels and silts present constraints (stoniness and compacity) for the roots.

Near the river, more groundwater passes through the organic horizons (Table 5), in all seasons in both zones. Thus, a higher proportion of the groundwater is affected by biological DIN removal. This enhances effectiveness of DIN removal in the forested riparian area. In spring 1999, the groundwater flow as well as the DIN mass entering the east zone is much higher than the west zone. Thus, DIN removal effectiveness is higher in the west zone than in the east zone, although rates of biological removal are lower.

In both zones, nitrogen removal is higher in early spring than winter (Table 4), although the water level is a little higher in January (about 10 cm, Fig. 4) and higher flows of groundwater are interacting with the microbiologically active layers. Our results involve water quality and concern only saturated layers of the soil, in which the denitrification rate remains stable through all seasons. In fact, the 'in situ denitrification rates', measured using the acetylene inhibition method of Yoshinari and Knowles (1976) by Cosandey et al. (2003b) in the organic layer, are equivalent in January 2000 and April 2000, respectively, 0.55 and 0.68 mg N per unit of soil weight (g) per day. (As April 2000 and April 1999 present equivalent hydraulic (Fig. 4) and climatic conditions (the averaged temperature of the sampled groundwaters are 7.3 and 7.8 °C, respectively), the measured denitrification rates have been assumed to be equivalent). Therefore, the differences observed between the two dates may correspond to the variation of plant uptake, which is maximal in spring in Swiss weather conditions. A similar seasonal variation of nitrogen removal was observed in a riparian wetland in Denmark (Brüsch and Nilsson, 1993), whereas both Simmons et al. (1992) and Nelson et al. (1995) observed the highest removal rates during the dormant season.

It is difficult to compare our DIN removal effectiveness with literature because the methodologies of calculation are different. Nevertheless, in both zones it seems to be low, especially in winter. For example, the winter nitrate retention was found to be 99% in a poplar vegetated riparian area and 84% in a grassed riparian area in UK (Haycock and Pinay, 1993). It was consistently high, above 80% during both growing and dormant seasons, in a wetland riparian area in Rhode Island (Simmons et al., 1992) as well as in a riparian area characterised by organic soils in New Zealand (Cooper, 1990). In these two cases, the groundwater flow corresponds to a very superficial lateral sub-surface flow, since the aquiclude layer occurs at depths lower than 2.0 m. Both a lower nitrate input and a greater proportion of groundwater flowing through the organic soils could explain the higher effectiveness in these riparian areas. Moreover, in our study site, the residence time of groundwater in organic layers is relatively low compared to other riparian wetlands. Hydraulic conductivities measured in these organic horizons (10^{-5}–10^{-4} m s^{-1}, Table 3) are 10–100 times higher than, for example conductivities (10^{-8}–10^{-6} m s^{-1}) measured by Devito et al. (2000) or those (10^{-7}–10^{-6} m s^{-1}) measured by Brüsch and Nilsson (1993).

4.2. Role of hydrogeological conditions

Interactions between groundwater and surface water in riparian areas are complex and their interpretation requires a comprehensive knowledge of the hydrogeological setting within the landscape (Devito et al., 1996; Branfireun and Roulet, 1998; Winter, 1999). Inadequate understanding of the hydrogeology in riparian areas generally limits the quantitative interpretation of study results (Correll, 1996).

The methodology we proposed and used to evaluate the effectiveness of riparian areas is based on the delimitation of stream tubes to construct water and nutrient mass balances. This methodology combines a good knowledge of the hydrogeological setting and a sound understanding of the aquifer geological structure. As demonstrated in our riparian area, the thickness of the aquifer formation can quickly vary between upslope and downslope, as well as laterally, and the water level is strongly time-variable. Combining knowledge of the area's geological structure with the piezometric maps permits the determination of groundwater thickness. This is an essential step before calculating groundwater flow and nitrogen mass in a riparian area. Moreover, the arrangement of the different layers composing the aquifer may also show considerable spatial variability. In our riparian area, for example, the organic horizon in the east zone is twice as thick as in the west zone. It is essential to take this into account when constructing mass balances, since the hydraulic properties of each layer are different. Moreover, the geochemical composition of the groundwater could vary between downslope and upslope, laterally as well as vertically. From such observations we were able to quantify the role of rain infiltration into the upper part of the aquifer, as well as estimate the amount of nitrogen input into the east zone. The basis of our methodology is to take into account heterogeneities in the hydrogeological system, observed during detailed fieldwork. This is all the more important since alluvial deposits, which are very heterogeneous, often characterise riparian areas. This high spatial variability characterises most natural environments. Therefore, we cannot consider a hydrogeological system via a bi-dimensional approach, assuming a horizontal, thin and homogeneous groundwater flow-path through riparian areas. We support the conclusions of Cey et al. (1999) and Devito et al. (2000), which emphasize the importance of understanding the three-dimensional organisation of groundwater flows in riparian studies. In this conceptual framework, monitoring must consider an area larger than the riparian site and vertical heterogeneities of the aquifer, in order not to omit any components of the hydrogeological system.

Our riparian area shows good effectiveness in removing nitrogen from groundwater owing to its specific geological structure. A large part of the groundwater is forced through biologically active horizons of the riparian area. Our methodology enabled us to verify and quantify this assumption since the water balance, and chloride balance, are equilibrated for the two zones. Our study showed that the effectiveness of a riparian area in biological removal is highly dependent on the pathway of water movement through biologically active layers of this area. At some sites, high denitrification activity occurs in saturated horizons characterised by low hydraulic conductivity. This means that these sites have little effect on riparian nitrogen removal because flow is minor in this low-conductivity material. On some sites, nitrate-rich groundwater may be transported in coarser sediments beneath lower-conductivity organic sediments for considerable distances across the riparian zone as shown by Hill et al. (2000). High effectiveness of a riparian area requires the combination of high biological removal, a considerable volume of groundwater flow and a high nitrogen flux through biologically active layers.

5. Conclusion

Our results emphasise the relevance of a three-dimensional approach to quantify the effectiveness of a riparian area in nitrogen regulation and therefore remediation of stream water quality. This is significant when managing floodplain environments for the reduction of non-point pollution.

For effective water-quality management, riparian areas must first be classified according to their potential effectiveness. This implies taking into account all fluxes recharging the river. Knowledge of the three-dimensional heterogeneity of sediments provides information on the hydrogeological setting of the riparian area. Sites with the highest potential effectiveness will correspond to those with the highest ratio of groundwater flow passing through the riparian area/total water flow recharging the river. Once the riparian area has been selected as a potentially effective riparian area, high-resolution soil and groundwater maps may be needed to locate layers which combine high biological removal and high nitrogen loads. Here, the use of spatialisation tools could help visualise the vertical and lateral distribution of these effective layers inside the riparian area.

These riparian areas often remain individualised entities within the landscape. They still have a permanent extensive cover such as forest or grassland. In fact, they correspond to wetland or hydromorphic land which were not easy to use with the former agricultural practices. As shown by our results, rain infiltration of these riparian areas may be as important as the groundwater flowing through them. Therefore, it is essential to maintain this non-nitrate-emissive use of riparian areas, in order to improve their dilution effect on the regulation of surface water quality.

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