Longitudinal transformation of nitrogen and carbon in the hyporheic zone of an N-rich stream: A combined modelling and field study

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ABSTRACT

A combined modelling and field study approach was used to examine biogeochemical functioning of the hyporheic zone in two gravel bars in an N-rich fourth-order stream (River Hers, south-west France).

Surface water and interstitial water were sampled monthly (August 1994–January 1995), the latter in a network of 29 piezometers in the first gravel bar and 17 in the second. In both gravel bars, the hyporheic zone was created only by advected channel water without any connection with groundwater. Longitudinal chemical profiles of Dissolved Organic Carbon (DOC), nitrate (NO_3–N), ammonium (NH_4–N) and Dissolved Oxygen (DO) were established for both gravel bars. Ambient and potential denitrification were measured in the laboratory during the same period using the acetylene inhibition technique. Factors limiting denitrification were also examined by testing the separate effects of nitrate or nitrate + carbon additions.

A 1D reactive-transport model was used to simulate longitudinal transformation of nitrogen in the hyporheic zone, and to estimate the role of organic matter (DOC and POC) in the biogeochemical functioning of the hyporheic zone.

Denitrification measurements with nitrate and nitrate + carbon additions both showed increased denitrification, suggesting that denitrification might not be C-limited at this site. Observations and model results showed the hyporheic zone to be a sink of DOC and nitrate, but DOC consumption appeared insufficient to explain nitrate depletion measured in the two gravel bars. Field data were better modelled when an additional DOC source from the POC fraction degraded by anaerobic respiration was included in the model.

1. Introduction

The hyporheic zone (HZ) is the area of saturated sediments beneath the stream bed and into the stream banks that contains some proportion of channel water (Findlay, 1995; Triska et al., 1989; White, 1993). The HZ is commonly defined as the zone that contains at least 10% stream water and less than 90% subsurface water (Triska et al., 1989). Research over the past two decades has established that the HZ has a great impact for stream ecosystem function and biogeochemistry (see reviews in Jones and Holmes, 1996; Brunke and Gonser, 1997; Boulton et al., 1998; Jones and Mulholland, 2000; Sophocleous, 2002; Birgand et al., 2007) because hyporheic exchanges enhance the mass transfer of dissolved solutes and particulates between the stream and the stream bed, which contains metabolically active microbial communities (Grimm and Fisher, 1984; Pusch and Schwoerbel, 1994; Sobczak et al., 1998; Sobczak et al., 2003). Flow patterns in the HZ create distinct gradients of physical and chemical conditions (Hendricks and White, 1991). Gradients between surface water and subsurface water develop by mixing of water with different physical and chemical characteristics and by biochemical processes in conjunction with the local residence time of water (Vervier et al., 1992; Brunke and Gonser, 1997). In particular, flow patterns may regulate the supply of oxygen and organic material to the HZ, thus influencing hyporheic metabolism and the processing of nutrients (Findlay et al., 1993; Jones et al., 1995; Boulton et al., 1998; Jones and Mulholland, 2000; Hinkle et al., 2001; Storey et al., 2004; Birgand et al., 2007).

Many studies have examined nutrient transformation processes in the hyporheic zone, with particular focus on nitrogen, and have shown that nitrogen dynamics operate quite differently in different stream systems (Duff and Triska, 1990; Jones et al., 1995; Holmes et al., 1996; Chestnut and McDowell, 2000; Hinkle et al., 2001;

Kasahara and Hill, 2006). A variety of factors can control nitrogen processing. For example, Holmes et al. (1996) showed that denitrification rates beneath a riffle of an Arizona desert stream were elevated at the head of the riffle by downwelling labile DOC, and were not inhibited by high oxygen levels in this zone. In contrast, Hill et al. (1998) found that denitrification in a lowland agricultural stream was limited by the rate of nitrate supply. Duff and Triska (1990) found a negative correlation between denitrification rates and DO along a transect away from a small forest stream. It thus appears that the factors controlling nitrogen processing differ among stream systems, probably due to differences in nutrient status and quality and amount of organic carbon (Storey et al., 2004). Other factors, such as sediment particle size (Jones 1995; Baker et al., 2000; Findlay and Sobczak, 2000) and temperature (Pusch, 1996), also potentially determine the types and rates of biogeochemical processes. However, despite the great number of studies describing nutrient and organic matter transformations along HZ flow paths, many challenges remain, such as the conditions that determine whether the HZ will be a source or a sink of nitrogen (Dent et al., 2000) and the role of organic matter quality for HZ metabolism (Butturini et al., 2000). One reason is that most investigations to date have focused on N-low streams (*e.g.* Triska et al., 1993; Holmes et al., 1996; Wondzell and Swanson, 1996), or on systems where the activity of nitrifying bacteria in HZ or ammonium-rich groundwater can provide a source of nitrate to surface water (*e.g.* Jones et al., 1995; Duff and Triska, 2000; Pretty et al., 2006).

In contrast to these studies where the HZ exports nitrate, Pinay et al. (1994), Hill et al. (1998), Storey et al. (2004), Lefebvre et al. (2006) and Kasahara and Hill (2007) found that the HZ in N-rich streams is a sink for nitrate arriving from the surface water. These results confirm the conceptual model of Jones and Holmes (1996), who proposed that low dissolved oxygen concentrations in the stream bed and high nitrate levels in the stream may result in a HZ that functions as a sink of nitrate where denitrification is the major nitrogen transformation process. The previous results also highlight the importance of comparing HZ functioning in different stream types (Stanley and Jones, 2000) and particularly the need for further studies in N-rich streams (Storey et al., 2004).

In this work, we addressed the dynamic of nutrients within the HZ by combining transport and biogeochemical activity in a modelling approach based on field study of an N-rich stream (River Hers, south-west France), where the HZ is created only by advected channel water (*cf.* White, 1993) without any connection with the groundwater. The model was applied to the data set: (1) to assess the role of transport and reactive processes in the longitudinal distribution of the chemical components in the HZ of the River Hers and (2) to estimate by numerical experimentation the rates of organic matter processing and the role of DOC and POC in the biogeochemical functioning of the HZ.

2. Study site

2.1. Location and hydro-geological context

The experimental site chosen was part of the River Hers (south-west France). It is a fourth-order stream tributary of the Garonne River, the third longest river in France (Fig. 1). The Hers provides a great opportunity to improve knowledge from less-studied stream types as it is an N-rich stream in which NO_3–N concentrations in surface water of 10 mg L^{-1} and more are common. The Hers watershed occupies an area of 972 km^2, and the river is 95 km long. The annual mean flow at the confluence with the Garonne is $4.13 \text{ m}^3 \text{ s}^{-1}$, with a value of $0.54 \text{ m}^3 \text{ s}^{-1}$ for low water periods and $52 \text{ m}^3 \text{ s}^{-1}$ for annual floods. The Hers is 20 m wide at the

study site and the mean water depth is about 2 m. The river flows over Garonne alluvia composed of elements from crystalline silts to gravels from the Pyrenees mountains (particle diameter 5–20 cm).

The site is located downstream from the confluence with the River Girou (Fig. 1A) near the confluence with the Garonne. Here, hydrological and morphological conditions are particularly adapted for the study of HZ biogeochemistry, since the river bed is located on a molassic substratum which disconnects the river and the HZ from groundwater inputs (Fig. 1B and C). The hyporheic zone is thus created only by advected channel water (*cf.* White, 1993) and consequently nutrient transformations in the HZ can be investigated without any influence of groundwater intrusion. The River Hers receives important quantities of peri-urban zone effluents and drains agricultural land. Water quality is thus poor, with high NO_3–N concentrations in surface water (10 mg L^{-1} and more) and high Chemical Oxygen Demand ($COD > 80 \text{ mg L}^{-1}$) and Biochemical Oxygen Demand ($BOD_5 > 25 \text{ mg L}^{-1}$).

2.2. Equipment

Two gravel bars (GB1 and GB2) were investigated for this study (Fig. 1B). In 1994, the site was equipped with a network of 29 piezometers in GB1 and 17 piezometers in GB2. Piezometers made from PVC (diameter: 4.5 cm) perforated along its entire length were introduced until the impermeable substratum (1–1.3 m depth) was reached. These piezometers were grouped by transects (5 transects for GB1 and 7 for GB2). Previous modelling works at this site have shown that flow in the two gravel bars is mainly longitudinal (Boly, 1997; Mear-Caubel, 2004). Piezometers in the same transect were thus considered to be replicates.

2.3. Field work

Patterns in nitrate (NO_3–N), ammonium (NH_4–N), Dissolved Organic Carbon (DOC) and Dissolved Oxygen (DO) were determined by measuring temporal data along the two gravel bars on five occasions at monthly intervals, from August 1994 to January 1995. Hydrology in the River Hers during the period was stable (Fig. 2) and corresponded to low water periods (discharge $1–7 \text{ m}^3 \text{ s}^{-1}$). Particulate Organic Carbon (POC) concentrations were also measured in the two gravel bars three months prior to this study (May 1994).

One litre of interstitial water was collected from each piezometer on each measuring occasion using a peristaltic pump. Water sampling commenced 10 min after the start of pumping in order to ensure that water chemistry was stable (monitored by oxygen concentration) and that only hyporheic water was sampled. Dissolved Oxygen was measured using a specific probe (WTW Multiline P4).

During the study period, ambient and potential denitrification rates were estimated by experimentation in the laboratory to determine the factors that control hyporheic denitrification in this stream. For denitrification measurements, sediments were sampled by vacuum pump on 26 July and 19 October 1994. All piezometers from A, B and C transects were sampled in GB1, and from transects K, L, M and N in GB2 (see Fig. 1). Sediments were also sampled through piezometers on the first day of the study period to estimate porosity.

2.4. Laboratory methods

Water samples for measurements of NO_3–N and NH_4–N were filtered through Whatman GF/F filters (nominal pore size 0.7 μm) prior to analysis. NO_3–N and NH_4–N concentrations were then determined using standard methods (NF T 90-015-2 and ISO 10
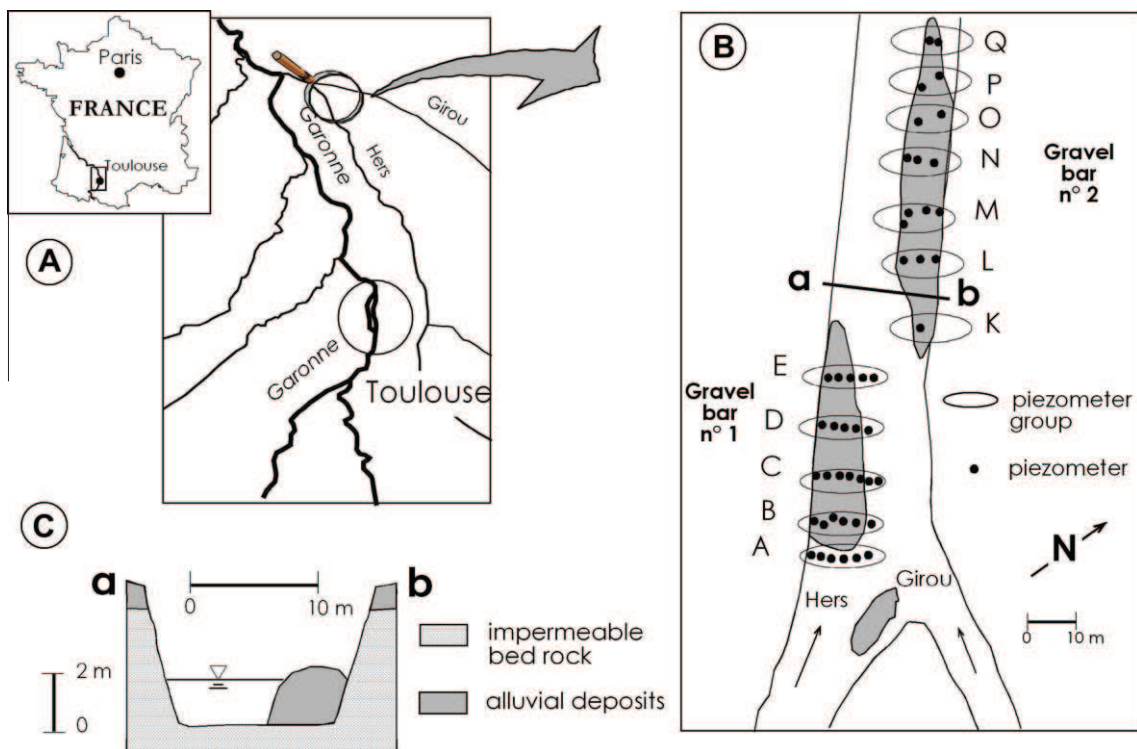
Fig. 1. (A) Location of the study site at the confluence of the Rivers Hers and Girou (43°45′53″N, 1°21′44″E), 20 km downstream from Toulouse (south-west France); (B) Schematic aerial view of the two gravel bars (GB1 and GB2) and location of piezometers; (C) Schematic cross-section of the river bed and GB2 along the a–b transect.
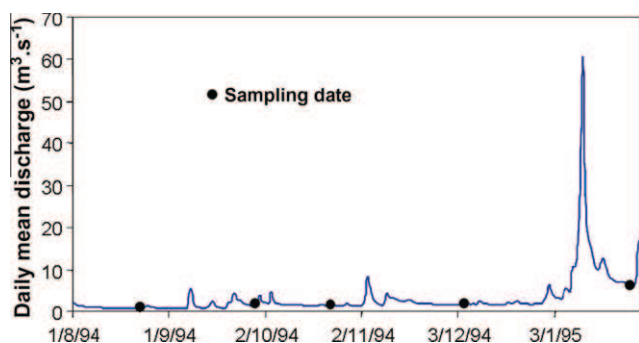

Fig. 2. Daily mean discharge of River Hers during the sampling experiment and sampling dates.

304 methods, respectively). Water samples for measurement of DOC were filtered using combusted GF/F filters (450 °C for 4 h) and analysed using a platinum catalyser at 650 °C (Shimadzu, Model TOC 5000).

Denitrification activity was estimated on sediment samples from the HZ using the acetylene block technique (Yoshinari and Knowles, 1976) to inhibit N_2O reduction to N_2 gas. Denitrification rates (ng NO_3–N removed $g_{sediment}^{-1}$ h^{-1}) in the HZ were determined by measuring N_2O production at *in situ* NO_3–N and carbon concentrations. Three replicates were made for each sampled piezometer. For each replicate, approximately 10 g of sediment (wet mass) were placed in a 250-mL serum bottle and then slurried with 10 mL of hyporheic water. Anoxic conditions were induced throughout the incubation by purging the 250-mL serum bottles containing sediment and HZ water slurries with industrial helium (99%) for 10 min before adding 25 mL of acetone-free acetylene gas to each bottle to yield 10% by total volume. The slurries were incubated for 24 h at 16 °C in the dark under moderate shaking. For each bottle, 3 mL of gas were sampled after 24 h and stored in vac-

uum tubes (Venoject; Terumo Scientific, NJ, USA) at room temperature until analysis. N_2O concentration was determined using a gas chromatograph (GIRDEL, Série 30, France) fitted with an electron capture detector (ECD 63Ni) and Porapak Q columns (2 m long packed columns).

Factors limiting denitrification were examined by measuring the separate effects of nitrate and nitrate + C-glucose additions. Three replicates were made for each sampled piezometer and for each experiment. To estimate the effect of nitrate, approximately 10 g of each sediment sample were placed in a 250-mL serum bottle and slurried with 10 mL of hyporheic water mixed with a $NaNO_3$ (100 mg N L^{-1}) solution. Denitrification Enzyme Activity (DEA) was determined by adding $NaNO_3$ (100 mg N L^{-1}) solution and glucose (50 mg C L^{-1}) solution to 10 g of sediment and 10 mL of hyporheic water. Mean denitrification was then calculated for each gravel bar using all piezometers for each experiment.

3. Numerical model

A 1D reactive-transport model was used as an exploratory tool to assess the role of transport and reactive processes in the longitudinal distribution of the chemical components, and to determine the role of organic forms (DOC and POC) in the HZ of the River Hers. The model presented here is a simplified adaptation of the model presented by Hunter et al. (1998), which was developed for subsurface environments. It incorporates four dissolved components (NO_3^-, NH_4^+, DOC and DO) and one solid component (POC).

3.1. Mass balance equation

The general mass conservation equation for dissolved components in the gravel bars is of conventional advection–dispersion-reaction form and can be written as:

$$\frac{\partial C_i^f}{\partial t} = -u\frac{\partial C_i^f}{\partial x} + D_i\frac{\partial^2 C_i^f}{\partial x^2} + R_i^f \tag{1}$$

where C_i^f is the concentration (μM) of the dissolved component i, u represents interstitial average flow velocity (m d^{-1}), D_i denotes the apparent/effective dispersion coefficient (m^2 d^{-1}, see Eq. (2)) and R_i is the reaction term (μM d^{-1}) for the component i. All concentrations used by the model are in μM but results in the following sections are in mg L^{-1}. Eq. (1) assumes that flow is uniform, permanent and one-dimensional. In this equation, D_i and u are considered to be spatially and time independent.The dispersion coefficient D_i is the result of the sum of the physical dispersion and the molecular diffusion of the dissolved components:

$$D_i = D_p + D_m^i \tag{2}$$

D_p is the physical dispersion (m^2 d^{-1}) and D_m^i denotes the effective molecular diffusion. D_m^i is generally in the order of 1–2×10^{-4} m^2 d^{-1}. Measurements showed the value of D_p for the site to be about 5×10^{-2} m^2 d^{-1}, and hence D_m^i can be considered negligible.

Following Hunter et al. (1998), the solid matrix was assumed to be immobile. Hence, the mass conservation equation for the solid component is:

$$\frac{\partial C_{poc}}{\partial t} = R_{poc} \tag{3}$$

where C_{poc} represents the POC concentration (mg g^{-1}) and R_{poc} is the reaction term (mg g^{-1} d^{-1}) for POC.

3.2. Reactions

The modelled reactions are presented in Table 1. In this paper, organic compounds are considered the source of energy for heterotrophic micro-organisms in the hyporheic zone. Organic matter is oxidised into inorganic molecules through microbial reactions. In the conventional presentation of biogeochemical models to date, these reactions are classified into two categories (Van Cappellen and Wang, 1995; Hunter et al., 1998; Wijsman et al., 2002): primary reactions (organic matter degradation pathways) and secondary reactions (microbial and chemical reactions using by-products of primary reactions). Moreover, these biogeochemical models incorporate mineralisation-precipitation reactions, acid dissociation reactions and adsorption processes. Here, available data did not allow a model as complex as that presented by Hunter et al. (1998) to be developed and applied, because this would have led to calibration of too many unknown parameters. Following the principles of simplicity and parsimony recommended in such modelling work (Burnham and Anderson, 2001; Johnson and Omland, 2004), a simplified view of the organic matter degradation processes was adopted by making several assumptions. Two organic forms were taken into account: dissolved organic carbon and particulate organic carbon. These forms were assumed to be degraded through three pathways: (1) aerobic mineralisation and nitrogen nitrification; (2) anaerobic degradation and nitrogen denitrification; (3) anaerobic degradation other than denitrification and ammonia release. Only nitrification was included as a secondary reaction. This model differs from that of Hunter et al. (1998) in number of organic degradation pathways (three versus five) and

number of secondary reactions (one versus ten). Following Soetaert et al. (1996), the final anaerobic degradation pathway was described as an holistic reaction term called 'anaerobic degradation' which accounts for manganese reduction, iron reduction and methanogenesis. However, neither the electron acceptors involved nor the re-oxidation reactions of their reduced form are explicitly included, which could lead to an underestimation of oxygen consumption. However, these re-oxidation reactions proved to have a weak influence on the final results because oxygen does not reach high concentrations in the HZ of the River Hers.

3.3. Kinetics

The multi-G modelling approach (Berner, 1980) was adopted. A general mineralisation rate was allocated to each form of organic carbon (DOC and POC), which could be modelled independently from the other compounds. The model calculates the relative contribution of each degradation pathway depending on the concentration of the various electron acceptors. Final anaerobic degradation occurs when O_2 and NO_3^- are consumed. First order kinetics were adopted as commonly used in studies of the hyporheic zone (e.g. Butturini et al., 2000) and of porous media in subsurface zones (Hunter et al., 1998). Saturation constants and inhibition constants were added to characterise the succession sequence of the degradation pathways. The general form for the limitation term is:

$$\frac{[EA_{\lim}]}{K_{EA} + [EA_{\lim}]} \tag{4}$$

where $[EA_{\lim}]$ is the limiting concentration (μM) of electron acceptor and K_{EA} (μM) is the limitation constant for the electron acceptor. It generates a decrease in the associated degradation process when the elector acceptor concentration decreases.

The inhibition term is written:

$$\left(1 - \frac{[EA_{in}]}{K'_{EA} + [EA_{in}]}\right) \tag{5}$$

where $[EA_{in}]$ is the inhibiting concentration of electron acceptor (μM) and K'_{EA} is the inhibition constant (μM) for the electron acceptor. It suppresses the latter reactions in the sequence by the occurrence of electron acceptors involved in the previous reactions. Rate laws for the reactions are given in Table 2 and model parameters are detailed in Table 3.

3.4. Numerical implementation

The partial differential equations (1)–(3) were solved using a Crank–Nicholson finite differencing scheme. We implemented this model resolution in a C code, using the developing platform Microsoft Visual C++ 2005 Express. The simulations were all transient simulations. The time step for numerical resolution was fixed at 10 min, and spatial resolution was 5 cm. For results, time step was 1 day and spatial resolution was 1 m. The conservation of matter was checked, and the accuracy and stability of the numerical solution were verified using analytical solutions for simplified test cases.

Table 1
Overview of the reactions included in the biogeochemical model. (1) Aerobic mineralisation; (2) Anaerobic degradation and nitrogen denitrification; (3) Aerobic nitrogen nitrification; (4) Anaerobic degradation other than denitrification and ammonia release. According to the Redfield ratio for organic matter, x = 106 and y = 16.

$(CH_2O)_x(NH_3)_y(H_3PO_4) + xO_2 \rightarrow xCO_2 + yNH_3 + HPO_4 + xH_2O$	(1)
$(CH_2O)_x(NH_3)_y(H_3PO_4) + 0.8xHNO_3 \rightarrow xCO_2 + yNH_3 + 0.4xN_2 + HPO_3 + 1.4xH_2O$	(2)
$NH_3 + 2O_2 \rightarrow HNO_3 + H_2O$	(3)
$(CH_2O)_x(NH_3)_y(H_3PO_4) + oxidant \rightarrow xCO_2 + yNH_3 + H_3PO_4 + xH_2O$	(4)

Table 2

Biogeochemical model formulations for each component. Parameter descriptions and values are given in Table 3.

$$R_{DOC} = -k_{DOC}\,[DOC]$$

$$R_{POC} = -k_{POC}\,[POC]$$

$$R_{O_2} = -\left(\frac{x+2y}{x}\right)\left(\rho\,\frac{1-\varphi}{\varphi}\,k_{POC}[POC] + k_{DOC}[DOC]\right)\frac{[O_2]}{K_{O_2}+[O_2]} - 2k_{NH_4^+}[NH_4^+]\frac{[O_2]}{K_{O_2}+[O_2]}$$

$$R_{NO_3^-} = -0.8x\left(\rho\,\frac{1-\varphi}{\varphi}\,k_{POC} = [POC] + k_{DOC}[DOC]\right)\frac{[NO_3^-]}{K_{NO_3^-}+[NO_3^-]}\left(1-\frac{[O_2]}{K'_{O_2}+[O_2]}\right) + k_{NH_4^+}[NH_4^+]\frac{[O_2]}{K_{O_2}+[O_2]}$$

$$R_{NH_4^+} = \frac{y}{x}\left\{\frac{[O_2]}{K_{O_2}+[O_2]} + \frac{[NO_3^-]}{K_{NO_3^-}+[NO_3^-]}\left(1-\frac{[O_2]}{K'_{O_2}+[O_2]}\right) + \left(1-\frac{[NO_3^-]}{K'_{NO_3^-}+[NO_3^-]}\right)\left(1-\frac{[O_2]}{K'_{O_2}+[O_2]}\right)\right\}\left(k_{DOC}[DOC] + \rho\,\frac{1-\varphi}{\varphi}\,k_{POC}[POC]\right)$$
$$- k_{NH_4^+}[NH_4^+]\frac{[O_2]}{K_{O_2}+[O_2]}$$

Table 3

Model parameter descriptions and values. (1) Boly (1997); (2) Mermillod-Blondin et al. (2003); (3) Vender *et al.* (1993) and Bernard et al. (1994); (4) Vender (unpublished data); (5) Wijsman et al. (2002); (C) Calibrated on data.

Variable	Unit	Value	Description
φ	–	0.34	Sediment porosity in the gravel banks (1)
ρ	kg dm^{-3}	1.3	Dry sediment density
D_P	M^2 d^{-1}	4.8×10^{-2}	Physical dispersion for solutes (2)
u	m d^{-1}	2	Mean advective velocity in gravel bars (3)
C_{POC}	mg g^{-1}	20	POC concentration in the gravel bars (4)
K_{DOC}	d^{-1}	0.68 (Simulation B)	Mineralisation rate constant of DOC (C)
K_{POC}	d^{-1}	0.06 (Simulation C)	
$k_{NH_4}^+$	d^{-1}	1.1×10^{-4} (Simulation C)	Mineralisation rate constant of POC (C)
	d^{-1}	0.01	Nitrification rate constant (C)
K_{O_2}	µM	3.1	Half-saturation for oxygen limitation in oxic mineralisation (5)
K'_{O_2}	µM	10	Half-saturation for oxygen inhibition (5)
$K_{NO_3}^-$	µM	30	Half-saturation for nitrate limitation (5)
$K'_{NO_3^-}$	µM	10	Half-saturation for nitrate inhibition (5)

4. Field application

4.1. Boundary conditions

Dissolved components enter the head of the gravel bars at $x = 0$, so the following boundary condition was adopted:

$$C_i^f = C_{i,0}^f \tag{6}$$

where $C_{i,0}^f$ denotes the concentration (µM) of component i measured at $x = 0$. Data in transects A and K were used as initial data at the boundary condition $x = 0$ for GB1 and GB2 respectively (see Fig. 1B). During the simulations, the concentrations of dissolved components at the head of the gravel bars were calculated using a linear interpolation between the concentrations measured at $x = 0$ on the different dates.

At the lower boundary, we assumed a no-gradient condition for the solutes:

$$\left.\frac{\partial C_i^f}{\partial x}\right|_{x=L} = 0 \tag{7}$$

where L represents the length of the gravel bar.

4.2. Initial conditions

Initial concentrations corresponded to the first sampling date (24 August 1994) and simulations were run for the four other dates. The initial concentrations along the gravel bars were calculated using a linear interpolation between the concentrations measured on the first sampling date in the different transects. In the simulations where POC was included (see the following section), the concentration of POC was considered constant along the longitudinal profile, and no new entry of POC occurred during the simulation period. Its concentration along the two gravel bars was fixed to 20 mg g$^{-1}_{\text{sediment}}$ (2%), as measured on 31 May 1994 (Vervier, unpublished data).

4.3. Model parameters

Parameters used for the reactions are summarised in Table 3. With respect to the reaction rates, we used limitation and inhibition constant values reported in Wijsman et al. (2002). The model provides 12 parameters to be fixed. Estimation of reaction rates strongly depends on the transport rates, and it appears unrealistic to calibrate both the transport and the reaction rates on a limited dataset. Values for some parameters were thus determined from the literature, or directly derived from data. At this point, three parameters remain to be calibrated with our data set: the constant rates of DOC and POC degradation (k_{DOC} and k_{POC}) and the nitrification rates ($k_{NH_4^+}$).

Physical dispersion was fixed to 4.8×10^{-2} m^2 d^{-1}, following the estimation of Mermillod-Blondin et al. (2003) in experimental gravel cores. Advective velocity was set to 2 m d^{-1}, as estimated from conservative tracer experiments by Vervier et al. (1993) and Bernard et al. (1994) in River Garonne gravel bars.

4.4. Simulations

To assess the possible role of POC and DOC in the biogeochemical functioning of the gravel bars, three modelling approaches were tested:

Simulation A. Reactive processes were set to zero and only the transport processes were considered, to assess how this affected the distribution of dissolved components along the longitudinal profiles.

Simulation B. Only DOC was accounted for and POC concentration was set to zero. The DOC mineralisation rate (k_{DOC}) was calibrated to obtain the best fit between model and output data, particularly for NO$_3$–N. In other words, we examined whether the DOC entering from surface water only could explain the nitrate consumption.

Simulation C. In this, DOC and POC were simulated. For each one, the mineralisation rates (k_{DOC} and k_{POC}) were calibrated to provide the best fit between model output and data.

5. Results

5.1. Field chemical results

Chemical measurements (Fig. 3) showed that NO_3–N concentrations in River Hers water were high during the study period (4.1–8.9 mg L^{-1}), whereas NH_4–N concentrations were relatively low (0.2–0.45 mg L^{-1}). In comparison, mean NO_3–N concentrations in hyporheic water were significantly lower (0.4–1.7 mg L^{-1}) and NH_4–N concentrations higher (1.1–2.5 mg L^{-1}) than in surface water. However, standard error values indicated that NO_3–N and NH_4–N concentrations in hyporheic water from both gravel bars presented a relatively high range of variation. This was mainly due to the longitudinal variations in these elements from upstream to downstream parts of the gravel bars. Indeed, NO_3–N concentrations (Fig. 3) showed a steep decline along the first metres of the hyporheic zone, decreasing by ~50–99% in GB1 and GB2. In parallel, the results show that NH_4–N concentrations (Fig. 4) were relatively stable or increased along the two gravel bars (by 22% in GB1 and by up to 413% in GB2).

Mean DOC concentrations (Fig. 3) were stable or tended to decrease during the study period in surface water (3.8 ± 0.2 mg L^{-1}) and tended to decrease in GB1 (from 3.9 to 2.9 mg L^{-1}). Longitudinal profiles along hyporheic flow paths for each sampling date also showed that DOC tended to decrease in GB1 (3.2 mg L^{-1} ± 20%) but remained generally stable (4.4 mg L^{-1} ± 8%) in GB2 (Fig. 5).

Dissolved Oxygen concentrations in Hers river water ranged from 9.4 to 11.2 mg L^{-1}, whereas hyporheic water in the field had very low concentrations (0.5 mg L^{-1} ± 19% in GB1 and 0.7 mg L^{-1} ± 23% in GB2) (Fig. 6).

To summarise, the surface water had high nitrate and oxygen concentrations and a low ammonium concentration, whereas hyporheic water had low nitrate and oxygen concentrations and a high ammonium concentration.

5.2. Denitrification measurements

Sediment slurry incubations for ambient conditions showed mean denitrification (±standard error) of 3.14 (±0.61, n = 21) ng NO_3–N removed $g_{sediment}^{-1}$ h^{-1} in GB1 and 1.85 (±0.23, n = 23) ng NO_3–N removed $g_{sediment}^{-1}$ h^{-1} in GB2 (see Fig. 7). Adding nitrate to samples increased denitrification to 13.43 (±1.72) and 8.78 (±2.05) ng NO_3–N removed $g_{sediment}^{-1}$ h^{-1} for GB1 and GB2 respectively. Similarly, nitrate plus carbon additions increased denitrifi-

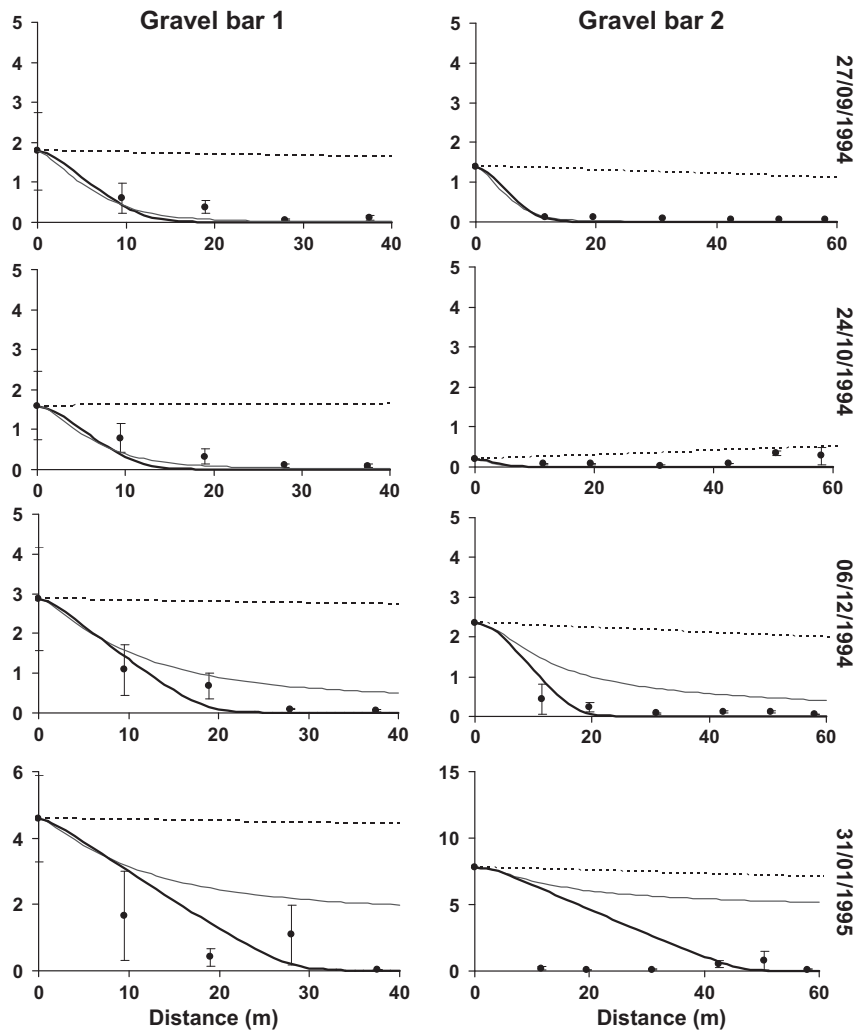**Fig. 3.** Measured (points) and simulated (curves) NO_3–N concentration (mg L^{-1}) profiles. Means and standard errors of measured concentrations are presented. Three modelling approaches are also presented: (A) only transport (dash line); (B) DOC representing the only source of carbon (solid grey line); (C) an additional source of POC added to DOC (solid black line).

Fig. 4. Measured (points) and simulated (curves) NH_4–N concentration ($mg\ L^{-1}$) profiles. Means and standard errors of measured concentrations are presented. Three modelling approaches are also presented: (A) only transport (dash line); (B) DOC representing the only source of carbon (solid grey line); (C) an additional source of POC added to DOC (solid black line).
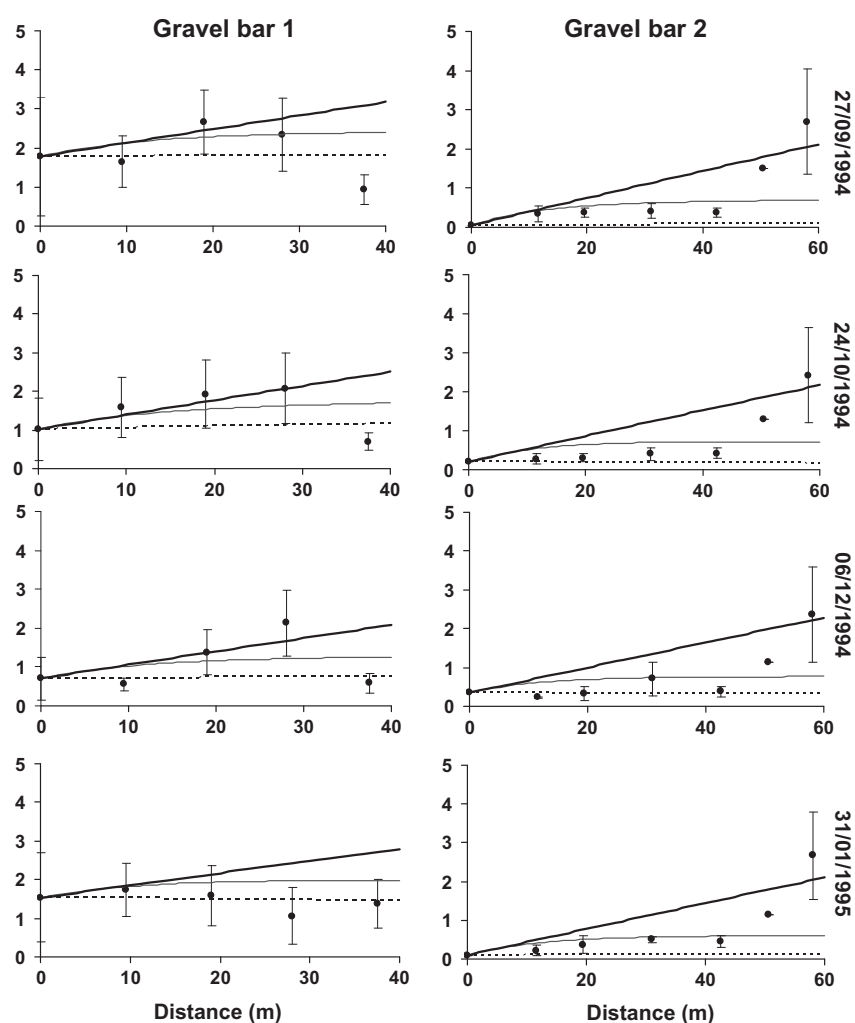
cation to 12.11 (±1.39) and 11.21 (±2.23) ng NO_3–N removed $g_{sediment}^{-1}\ h^{-1}$ in GB1 and GB2 respectively. Compared to nitrate addition alone, nitrate plus carbon addition did not give rise to a significant additional increase in denitrification (ANOVA, ns). Nitrate is thus a limiting factor for denitrification reactions in the two gravel bars, whereas organic carbon is not.

5.3. Model results

5.3.1. Simulation A (conservative transport)

As expected with this simulation, the modelled concentrations of NO_3–N, NH_4–N, DOC and DO were quasi-homogeneous along the longitudinal profiles of GB1 and GB2 (see Figs. 3–6 respectively). This is due to the constant mean porewater advection ($2\ m\ d^{-1}$) and the absence of gross variation in concentrations on entering the gravel bars. In most cases, transport alone could not explain the longitudinal distribution of the chemical components, particularly for the measured NO_3–N profiles (Fig. 3), which always showed an exponential decrease along the gravel bars. Except in GB1 on 31 January 1995, measured NH_4–N concentrations (Fig. 4) showed an increasing trend in all profiles that was not reproducible with transport only. As regards the DOC concentrations (Fig. 5), the modelled concentrations were slightly overestimated in GB1, where the measured concentrations tended to

decrease, whereas they were underestimated in GB2, where the measured concentrations were generally stable or increasing. The case of DO (Fig. 6) was more sensitive, because the transport only seemed to be sufficient to explain the longitudinal concentrations. However, note that with our measurement procedure (water pumped up from piezometer, then probe plunged inside sample), it was not possible to determine whether these concentrations were significant or due to empirical errors (see discussion below).

5.3.2. Simulation B (reactive transport with DOC and without POC)

The main discrepancy was in the shape of the simulated profiles, in that whereas measured concentrations of the four components showed peaks and sometimes strong variations among the piezometers, the model provided highly smooth shapes and trends in the simulated profiles. This is a consequence of the assumption of homogeneous transport and reactive processes along the gravel bars, where in fact the actual physio-chemical conditions are probably longitudinally heterogeneous. Nevertheless, simplification is the foundation of any modelling exercise and in the present case, despite this assumption, the model provided important insights about biogeochemical functioning within the HZ.

The estimation of model parameters was optimised to provide the best fit for NO_3–N profiles. With DOC as the only source of organic matter and with a degradation coefficient of k_{DOC} = 0.68 d^{-1},
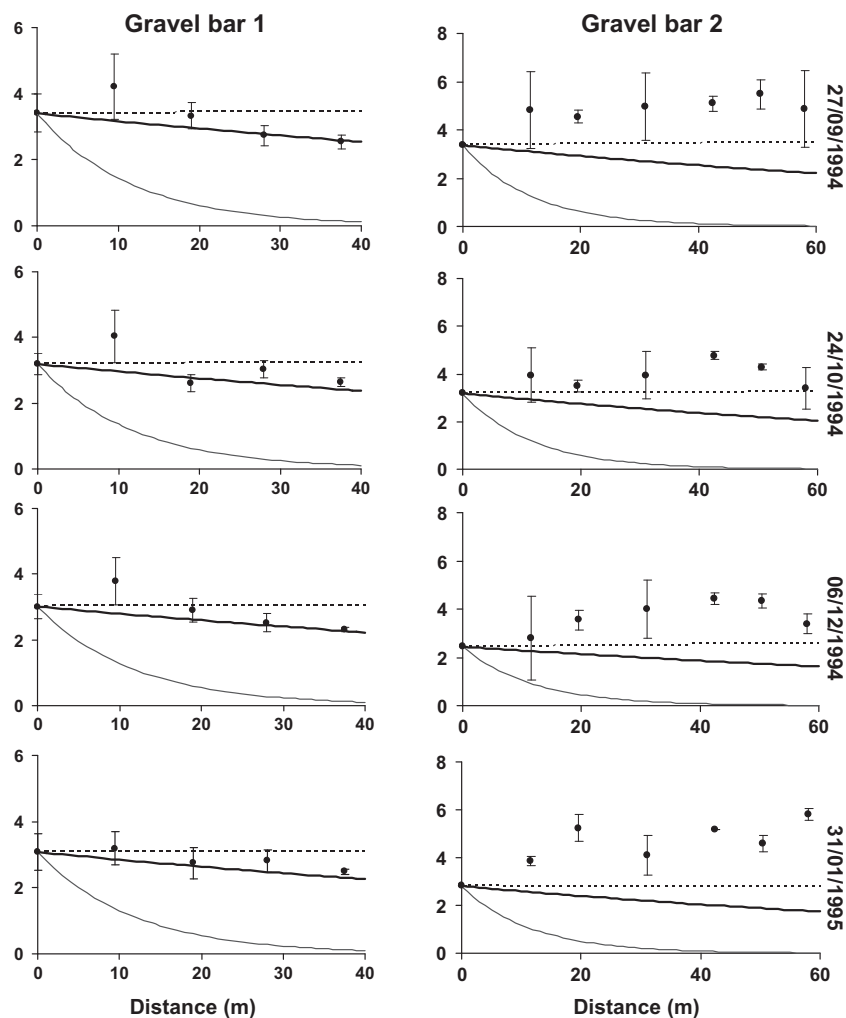
Fig. 5. Measured (points) and simulated (curves) DOC concentration (mg L^{-1}) profiles. Means and standard deviations of measured concentrations are presented. Three modelling approaches are also presented: (A) only transport (dash line); (B) DOC representing the only source of carbon (solid grey line); (C) an additional source of POC added to DOC (solid black line).

the model fitted the measured concentrations of NO$_3$–N in GB1 and GB2 reasonably well on 27 September 1994 and 24 October 1994 (Fig. 3), but overestimated it on 6 December 1994 and 31 January 1995. The simulated NH$_4$–N profiles showed an increasing trend along the gravel bars, the pattern was in accordance with the measured concentrations even though the actual values were greatly underestimated. Conversely, forcing the fit of the nitrate profile made the model strongly underestimate the DOC concentrations. The simulated profiles showed complete consumption of DOC after 40 m in both GB1 and GB2, whereas the measured concentrations were still between 2.3 and 2.6 mg L^{-1} in GB1 and between 3.3 and 5.8 mg L^{-1} in GB2 at the end of the gravel bars. The complete consumption of DOC after 40 m coupled to the highest nitrate concentrations on 6 December 1994 and 31 January 1995 explain why the simulated NO$_3$–N concentrations were overestimated on these dates in GB1 and GB2 – there was no more DOC available to be degraded by denitrification and to consume the nitrate. This important result means that DOC is not a sufficient source to explain the NO$_3$–N consumption within the gravel bars. Regarding DO profiles (Fig. 6), the model showed complete disappearance of DO along the first metres of the gravel bars, whereas measured concentrations were not zero (but very low) at any point along the longitudinal profiles.

The modelled mean denitrification rates (±standard error) calculated from the simulations (as already mentioned in the Methods section, the multi-G approach does not allow denitrification to be imposed but deduces it from the reaction system) were 2.41 (±0.01) ng NO$_3$–N removed $g_{sediment}^{-1}$ h^{-1} in GB1 and 1.49 (±0.03) in GB2. These values are slightly lower than the measured ambient denitrification rates for GB1 and GB2 (respectively 3.14 and 1.85 NO$_3$–N removed $g_{sediment}^{-1}$ h^{-1}, see Fig. 7).

5.3.3. Simulation C (reactive transport DOC and POC)

As with simulation B, the simulated profiles were of a smooth nature. Again, as in simulation B, the organic carbon degradation rates were fixed to optimise the fit of the NO$_3$–N profiles. With $k_{DOC} = 0.06$ d^{-1} and $k_{POC} = 1.1.10^{-4}$ d^{-1}, the model fitted the NO$_3$–N profiles reasonably well, and a noticeable improvement appeared compared to simulation B, particularly for 6 December 1994 and 31 January 1995. In the same manner, the model better reproduced the general trend for an increase in the NH$_4$–N profiles in GB1 and GB2. Regarding DO, the findings were similar to those for simulation B.

For the denitrification rates, the model provided higher values than with simulation B: 2.98 (±0.07) ng NO$_3$–N removed $g_{sediment}^{-1}$ h^{-1} in GB1, and 2.62 (±0.08) in GB2.
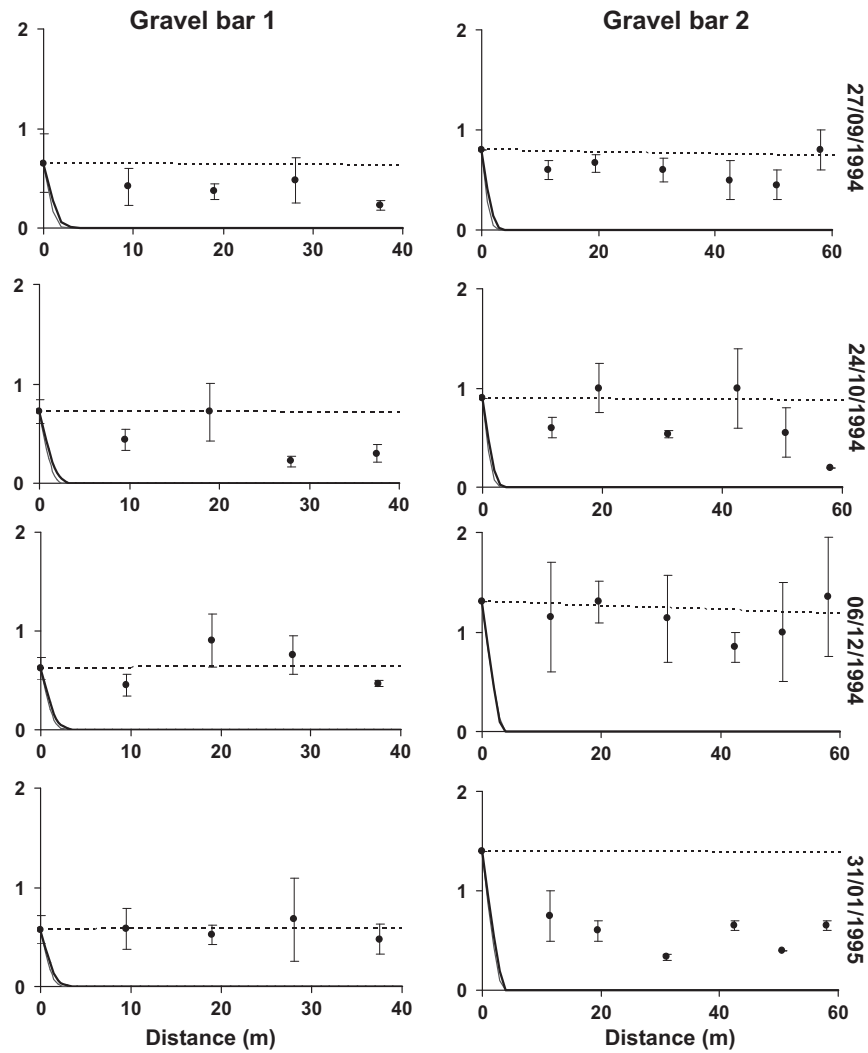
Fig. 6. Measured (points) and simulated (curves) DO concentration (mg L^{-1}) profiles. Means and standard deviations of measured concentrations are presented. Three modelling approaches are also presented: (A) only transport (dash line); (B) DOC representing the only source of carbon (solid grey line); (C) an additional source of POC added to DOC (solid black line).

Lastly, and this is an important point, the DOC concentrations were correctly simulated in GB1, with a slight decrease along the gravel bar, and better simulated in GB2, even though the increasing trend with distance from upstream to downstream was not reproduced. This confirms the necessity of an additional source of organic matter to DOC (POC here) to explain the denitrification processes.

6. Discussion

6.1. Nitrogen transformation in the hyporheic zone

In natural systems, declines in NO$_3$–N concentrations along the hyporheic zone may be the result of dilution from additional water sources (*e.g.* groundwater, tributaries, etc.) or of biological processes such as microbiological denitrification, vegetative uptake or microbial incorporation (Pinay et al., 1998; Sobczak et al., 2003). At the site investigated in the present study, dilution can be excluded as a potential mechanism for NO$_3$–N losses since the hyporheic zone is disconnected from the groundwater. As there was no highly developed vegetation on either gravel bar, vegeta-
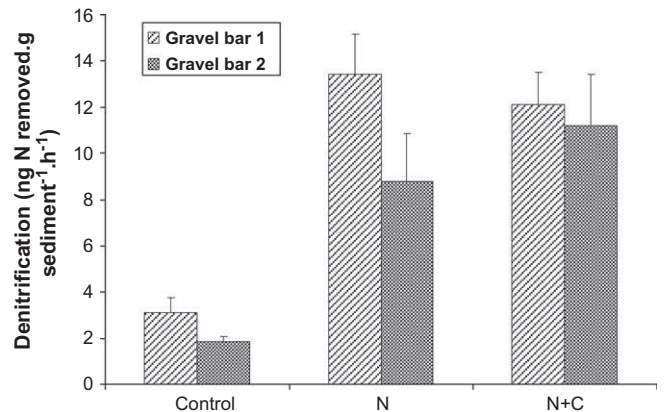

Fig. 7. Denitrification rate measurements (ng N removed g$^{-1}_{sediment}$ h^{-1}) in Gravel Bar 1 (GB1) and Gravel Bar 2 (GB2) with NO$_3$–N addition and with NO$_3$–N + C addition compared with the control experiment without addition (control). Means and standard error bars are presented for all GB1 and GB2 data (n = 21, n = 23 respectively).

tive uptake can also be excluded. The NO$_3$–N and DO concentrations in the River Hers were more than 4.1 and more than 9.4 mg L^{-1} respectively. However, stream water entering the gravel bars showed a rapid decline in NO$_3$–N within a short distance and a strong decrease in DO, generally to under 1 mg L^{-1} (Fig. 3). These patterns indicate a strong redox gradient in the hyporheic zone and suggest the occurrence of aerobic microbial respiration followed by denitrification (Hedin et al., 1998). Denitrification measurements and NO$_3$–N losses through hyporheic flow paths indicate that this process appears to very important in the assimilative processes in the River Hers. As reported for other N-rich systems (*e.g.* Hill et al., 1998; Storey et al., 2004), measured denitrification rates were limited by the rate of nitrate supply, whereas organic carbon did not seem to be an important factor in the hyporheic zone of the River Hers. However, simulations showed that NO$_3$–N longitudinal profiles were better reproduced by the model when a source of POC was added (see section on Simulation C above). For simulations B and C, simulated denitrification rates are close to measured denitrification and, in view of model simplifications and as the denitrification was not measured directly *in situ*, the slight differences between observations and predictions were expected.

Despite the simplicity of the model, its outputs fitted measured NO$_3$–N and NH$_4$–N data reasonably well, particularly with simulation C. Concentration profiles of NO$_3$–N (Fig. 3) adopted an exponentially decreasing shape, denoting consumption through the denitrification process, except on 31 January 1995, where the influence of a previous flood event (Fig. 2) was probably non-negligible (NO$_3$–N concentration up to 35 mg L^{-1} at the head of GB2). The hyporheic zone at this site is thus an NO$_3$–N sink, rather than a source, in agreement with results from other N-rich streams (Pinay et al., 1994; Hill et al., 1998; Storey et al., 2004; Kasahara and Hill, 2006 and 2007), and fits the conceptual framework of Jones and Holmes (1996). In contrast, NH$_4$–N concentrations increased along the longitudinal gradient (Fig. 4). The DOC concentration being relatively stable along the gravel bars (Fig. 5), these converse ammonium and nitrate concentration gradients suggest that the hyporheic zone supports coupled nitrification–denitrification, where a part of ammonium comes from nitrate ammonification. Some studies have also reported an ammonium increase in the hyporheic zone due to Dissimilatory Nitrate Reduction to Ammonium (DNRA) (Storey et al., 2004). In the case of the River Hers, DNRA does not seem to be possible because nitrate concentrations fell quickly along the first metres of the gravel bars and there was no more nitrate available for DNRA in downstream parts. The increase in ammonium at the end of GB2 is undoubtedly attributable to particulate organic matter (POM) desamination (see last paragraph in Simulation C section above). This nitrate-derived ammonium was first oxidised into nitrate, then subsequently reduced *via* denitrification into N$_2$ (Sheibley et al., 2003). This is apparent in Fig. 8 for GB1, where the total mineral nitrogen content fell by more than 75% between the upstream and the downstream parts of the gravel bar. On the other hand, in GB2, after a loss of almost 80% of total mineral nitrogen content, there was an increase by which it became practically equivalent to the mineral nitrogen content of the first transect. This increase in total mineral nitrogen was due to an increase in ammonium content and, the nitrate content being very low, the organic matter remains the only ammonium source. This source of ammonium for surface water could have a large impact on stream functioning, since this form of nitrogen is that most consumed by river micro-organisms (Webster et al., 2003).

With both simulations B and C, the simulated DO concentrations were very low and uniform in the gravel bars (0.5–1.1 mg L^{-1}), and the model considered this DO to be rapidly consumed. However, measured concentrations of oxygen along the longitudinal gradient were non-null, even if low, and relatively
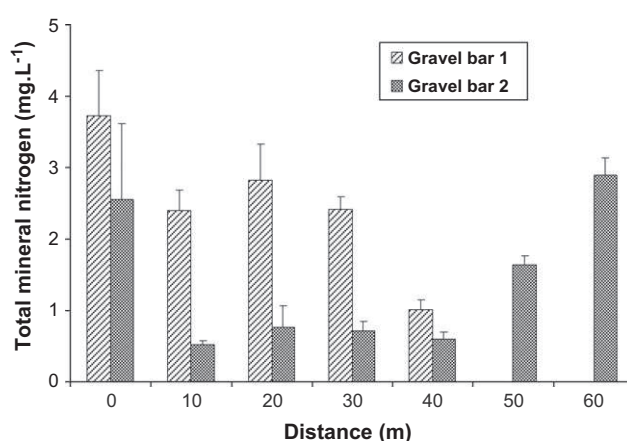

Fig. 8. Mean (+standard error) total mineral nitrogen (nitrate + ammonium) losses (mg L^{-1}) in gravel bars 1 and 2, from upstream to downstream piezometers, during the 6-month study.

constant. This could not be the result of lateral inputs of water into the gravel bars, as the hyporheic flow of the River Hers is primarily longitudinal and disconnected from groundwater. However, it should be noted that the measured concentrations were close to anoxic conditions and with our measurement procedure (water pumped up from piezometer, then probe plunged inside sample), it was impossible to determine whether these concentrations were significant. It is probable that oxygen was reintroduced into samples during this manipulation and that the probe worked close to its limit of detection. An accurate determination of oxygen content in anoxic water requires the use of *in situ* measurements (*e.g.* micro-sensors) in order to prevent any atmospheric oxygen contamination of the sample. Such denitrification processes, even when some oxygen is still present, have been observed in previous studies of the hyporheic zone and groundwater (*e.g.* Vervier et al., 1993; Holmes et al., 1996; Schramm et al., 1996; Sánchez Pérez et al., 2003). Since denitrification by most bacteria is inhibited by oxygen concentrations above 0.3 mg L^{-1} (Tiedje, 1988), studies of the hyporheic zone have all concluded that denitrification must be occurring in small pockets of anoxic conditions (Storey et al., 2004), which may form in low permeability sediments where water turnover is low (Baker et al., 2000) or in deposits of Particulate Organic Matter where respiration is high (Duff and Triska, 1990). Another explanation could be that aerobic respiration in the outer layers of bacterial biofilms can produce anoxic conditions in the inner layers, allowing denitrification despite oxic conditions in the overlying water (Vervier et al., 1992; Schramm et al., 1996).

6.2. Comparison with other streams

Most previous studies have been carried out at sites with low surface water NO$_3$–N (*e.g.* 0.02 mg L^{-1}, Triska et al., 1993; 0.099 mg L^{-1}, Jones et al., 1995; 0.15 mg L^{-1}, Valett et al., 1996; less than 0.01 mg L^{-1}, Wondzell and Swanson, 1996) relative to the River Hers (4.1–8.9 mg L^{-1} during the study period). In most of these studies, dissolved oxygen (DO) remained relatively high throughout the hyporheic zone (3.9 mg L^{-1}, Jones et al. 1995; 5.5 mg L^{-1}, Wondzell and Swanson, 1996), and nitrate increased along subsurface flow lines (from 0.099 to 0.173 mg L^{-1}, Jones et al., 1995; from 0.01 to 0.02 mg L^{-1} along gravel-bar flow line in summer, Wondzell and Swanson 1996). On the contrary, in the River Hers, nitrate and DO decreased to very low levels in the hyporheic zone and ammonia tended to increase, particularly in GB2. Many factors could explain such functioning. First, as interstitial flow velocities in the gravel bars were relatively low (2 m d^{-1}),

hyporheic microbial activity had enough time to remove oxygen from the inflowing water. Second, relatively high and constant DOC concentrations along the hyporheic zone provided substrate for respiration, causing rapid oxygen uptake. Compared with denitrification, nitrification seems to be of minor importance in the River Hers, probably because of relatively low concentrations of ammonium brought in by surface water. The relative importance of nitrification as a source of nitrate was further decreased by the very high concentrations of nitrate in inflowing surface water. Denitrification, in contrast, was of major importance. Denitrification rates in the River Hers were lower than the 4–7 ng N removed $g_{sediment}^{-1}$ h^{-1} reported by Holmes et al. (1996) but very close to values estimated by Storey et al. (2004) for the River Speed (average 0.46–1.96 ng N removed $g_{sediment}^{-1}$ h^{-1}), and by Sánchez Pérez et al. (2003) and Iribar (2007) in River Garonne sediments (average from about 2.1 to 4.9 ng N removed $g_{sediment}^{-1}$ h^{-1}).

We also noted a large unused potential for denitrification in the hyporheic zone of the River Hers. Indeed, adding nitrate or nitrate plus carbon to samples multiplied denitrification rates by about fivefold. However, compared with nitrate addition, nitrate plus carbon addition did not give an additional increase in denitrification. It thus seems that carbon is not limiting in the two gravel bars, as denitrification rates were similar with or without addition of carbon, but that denitrification is limited by nitrate. This point was underlined by Hill et al. (1998), who found that denitrification in an agricultural stream was limited by the rate of nitrate supply. Laboratory measurements and field observations by Storey et al. (2004) led them to the same conclusion regarding the River Speed.

6.3. Role of DOC and POC

A major result emerged from comparison of DOC profiles produced by simulations B and C (Fig. 5). In simulation B, the model output showed an exponential decrease in DOC concentration along the longitudinal gradient that completely differed from the measured data. In simulation C, the decrease in DOC concentration was low and the model accurately fitted the data for GB1 but not for GB 2, where DOC concentrations slightly increased along the bar. In addition, simulation C better simulated NO_3–N profiles for 6 December 1994 and 31 January 1995 (Fig. 3). This result showed that the amount of DOC entering from the surface water was not sufficient to explain the NO_3-N consumption by denitrification. The gravel bar metabolism may also use another source of organic carbon, represented here by the POC. It is now recognised that only a fraction of the DOC transported in streams is available for hyporheic bacterial uptake, and particulate organic carbon (POC) into the sediments can represent an additional source of DOC (Mulholland 1981; Sobczak et al., 1998; Schindler and Krabbenhoft, 1998). Organic matter in sediments can thus have many different possible origins: allochthonous organic matter can be buried in sediments during episodic high discharge (flood pulses, cf. Junk et al., 1989) or result from degradation of dead organisms or from dissolved organic matter adsorption and microbial assimilation into biofilms. After hydrolysis, this hyporheic organic matter could represent an additional source of DOC in the hyporheic zone. The relative contribution of DOC and POC to sedimentary microbial communities changes temporally and spatially in different riparian habitats (Sobczak et al., 1998). For example Brugger et al. (2001) showed that POC controls the distribution of microbial metabolism within the riparian zone of streams and that POC may be the main source of carbon for interstitial bacteria. Heterotrophic organisms in stream and river sediments depend largely on organic matter. The metabolism of hyporheic bacteria has thus been found to be related to the input of particulate (POC) or dissolved organic carbon (DOC) from the surface (Hedin, 1990; Findlay and Sobczak, 1996; Fischer et al., 1996). Hyporheic bacteria are thus often more

abundant and exhibit higher activity in downwelling than in upwelling regions (Fischer et al., 1996; Storey et al., 2004). The origin of POC in the gravel bars of the River Hers is unclear but there are indications that it is stored in sediments during floods and slowly consumed when DOC content is not sufficient to sustain hyporheic metabolism.

The mineralisation rate of DOC calculated in simulation C (k_{DOC} = 0.06 d^{-1}, or $T_{1/2}$ = 11.5 d) is in accordance with natural values. For example, Matsumoto (1983), using two first order equations, measured the following degradation constants for DOC: k_1 equal to 0.066 d^{-1} ($T_{1/2}$ = 10.5 d) in the River Tama (Japan), close to our value in simulation C, and a k_2 between 0.0056 and 0.0075 d^{-1} ($T_{1/2}$ = 124 d), which corresponds to constants for natural refractory organic matter. Wetzel and Manny (1972), using a double exponential function, calculated degradation constants k_{2DOC} = 0.009 d^{-1} (or $T_{1/2}$ = 80 d) for leaf leachate from hickory (*Carya glabra*) and maple (*Acer saccharum*). In comparison, the mineralisation rate of DOC calculated in simulation B (k_{DOC} = 0.68 d^{-1}, corresponding to a half-life time $T_{1/2}$ = 1.02 d) is high and corresponds to highly reactive material, which may appear unrealistic in such hyporeic environment.

The calibrated kinetics constant for particulate organic carbon (k_{POC} = $1.1.10^{-4}$ d^{-1}) in the River Hers is very low according to the Petersen and Cummins (1974) classification (Group I: slow degradation group, k less than 5.10^{-3} d^{-1}). Melillo et al. (1983) calculated k_{POC} = 10^{-4} d^{-1} for woody fragments of *Picea mariana* in the well-oxygenated River Moisi (Canada), which is comparable to our results. The low value in the present study could be attributed to the refractory nature of particular organic matter, and to the relatively fine size of the particles in the gravel bars. The smaller the size of the particles, the lower the value of the constant k. Indeed, the smallest fractions are the more processed organic matter, of which the easily biodegradable part is already eliminated (Koutny and Rulik, 2007).

7. Conclusions

In this work, we confirmed that for N-rich streams, the hyporheic zone is a sink of nitrate. We also showed that denitrification potential in the hyporheic zone was high and was limited in the field by the rate of nitrate supply. With the modelling approach adopted, we were able to propose a hypothesis to express the complexity of functioning of the hyporheic zone. In particular, we explored the relationships between DOC and POC by proposing degradation rates of DOC and transformation rates from POC to DOC. From the results, we can also deduce that this model could be improved by better descriptions of transport and medium heterogeneity.

It emerged that to integrate the role of the hyporheic zone in the functioning of a running water system by a modelling approach, it is essential to test the relative role of transport and the heterogeneity of the hyporheic zone and to integrate the biogeochemical system-related POC, DOC and denitrification processes.

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