River bank filtration: modelling of the changes in water chemistry with emphasis on nitrogen species

Claude Doussan [a,*], Guillemette Poitevin [b], Emmanuel Ledoux [b], Michel Detay [c]

[a] *INRA, Unité de Science du Sol, Domaine Saint Paul, Site Agroparc, F-84914 Avignon Cedex, France*
[b] *Centre d'Informatique Géologique, École des Mines de Paris, F-77305 Fontainebleau, France*
[c] *Lyonnaise des Eaux, F-49300 Cholet, France*

Abstract

Bank-filtrated water is an important component of the drinking water production in many countries. The changes in the water chemistry during the transfer from the river to the aquifer have important implications for the quality of the produced water. In this paper, we first describe certain features of the evolution of the water chemistry during bank-filtration in the case of an experimental site, part of a large well field (Seine river, France). Here, bank-filtration leads to highly reducing conditions in the aquifer. A conceptual and numerical macroscopic model of this evolution, focusing on nitrogen compounds, is then presented. The model is designed to simulate organic matter mineralization and redox reactions catalyzed by bacteria in the river bed sediments where water infiltrates. Growth and decay of bacteria are explicitly accounted for and a numerical solution is found with an operator splitting technique. The model is able to reproduce column experiments by von Gunten and Zobrist (1993) designed to simulate infiltration of organically polluted river water into an aquifer. A model application to the characteristics of the experimental site is also presented. Results of a sensitivity analysis highlight the importance of: (1) the flow rate of water infiltrating river bed sediments; and (2) the organic carbon content of these sediments, for the evolution of the water quality during transfer from the river to the aquifer. © 1997 Elsevier Science B.V.

Keywords: Groundwater; Denitrification; Ammonification; Model; Bacteria; Sediments

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* Corresponding author.

1. Introduction

In many countries alluvial aquifers hydraulically connected to a water course are preferred sites for drinking water production. Since these aquifers are relatively easy to exploit (shallow), generally highly productive and located close to the consumers. In France, for instance, the proportion of bank-filtrated water amounts to ~ 50% of the total drinking water production (Castany, 1985). However, because of their location, their shallowness and their close relationship with the water course, these aquifers are particularly sensitive to pollutants (Schwarzenbach et al., 1983). For example, since these aquifers are often already threatened by agricultural nitrates, the impact on the groundwater quality of an increase in nitrogen species in the river water is a problem which should be addressed.

There are few models describing transport between a river and a contiguous alluvial aquifer influenced by pumping. Gilliland and Nguyen (1987) have presented a model dealing with nitrate contamination of an alluvial aquifer strip extending from a river to a pumping well. The groundwater is vertically stratified with nitrate from the river. In this case, the nitrate is assumed to be conservative and transported by convection into the aquifer. Laszlo and Szekely (1989) offer a more detailed model focused on the behavior of iron and manganese and, to a lesser extent, nitrate. The evolution of the chemistry of percolating water is represented by a succession of redox reactions for which the basic assumptions are:

(1) succession of reactions in order of decreasing redox potentials;

(2) switching from one reaction to another after complete exhaustion of the oxidizing agent;

(3) instantaneous reactions.

The flow field is at steady state. Iron concentrations measured in a well field located along the Danube river show relatively good agreement with the modeled ones. For nitrate, the agreement is less clear. Matsunaga et al. (1993) have also modeled Fe, Mn, and some other species in a system consisting of a column filled with river sediments. The evolution of the filtrate chemistry is similarly represented by a set of redox reactions and the local equilibrium assumption is formulated for dissolved species. Nitrate and organic matter are considered in these reactions. The authors show, in particular, that the decomposition rate of organic matter has a major influence on the resulting equilibria.

In these models, the influence of the microflora, naturally occurring in the river sediments and the aquifer is not, or only indirectly, taken into account. In fact, microbiological activity plays a key role in the evolution of the water chemistry during the transfer from the river to the aquifer (Jacobs et al., 1988; Gounot and Di-Ruggiero, 1991; von Gunten and Lienert, 1993; Doussan, 1994). The bacteria catalyze many redox reactions involving organic matter in conjunction with an electron acceptor. The latter is often a mineral compound (oxygen, nitrate, Fe- and Mn-oxyhydroxides, etc.) but it could also be an organic molecule (fermentative metabolism). All these processes can act simultaneously during river–aquifer transfer (von Gunten and Zobrist, 1993). In this way, bacteria obtain energy for metabolic processes and carbon for construction of their cellular material. The geochemical context of river–aquifer transfers and its evolution is

then a reflexion of interactions between biological and physico-chemical mechanisms. In addition to influencing the chemistry, the bacterial activity may affect the hydrodynamic parameters of the porous medium. For example, Taylor and Jaffé (1990), as well as Cunningham et al. (1991), show that the growth of a bacterial biofilm may significantly alter the porosity and permeability of the porous medium, which might result in the clogging of the river banks, especially at the river–sediment interface where the bacterial activity is high.

Over the past few years, numerous models have been built to simulate reactive transport in groundwater. The most recent innovation, notably due to the development of bioremediation techniques, is the explicit representation of biologic activity in the porous medium and its effects on the fate of different compounds (Baveye and Valocchi, 1989; Odencrantz et al., 1990; Semprini and McCarty, 1991; Chen et al., 1992; Brian et al., 1994).

It is generally shown that most of the bacteria are fixed on the solid phase in aquifers (Kobel-Boelke et al., 1988; Harvey et al., 1989) or in river sediments (van Beelen and Fleuren Kemila, 1989). There are several reasons for this (Martin, 1985), for example:

(1) Easier access to nutrients, because solid organic matter may be a direct substrate; it can also concentrate the dissolved nutrients because of its adsorbing properties.

(2) Formation around bacteria of micro-zones of polysaccharidic gels and other bacteria. This zone limits the dispersion of the metabolites and nutrients. It may also protect the microorganisms against desiccation or phagocytosis, toxins, etc.

This conglomerate, consisting of the fully hydrated polymeric gel and bacteria, is called biofilm. Solute movements are restricted in the biofilm phase (Baveye and Valocchi, 1989). The presence and extent of this diffusion barrier has led to different kinds of models available in the literature and describing bacterial activity. In one type of model, the diffusion barrier is neglected (because it is very thin) and bacteria reach the substrates directly by advective–dispersive transport (Srinivasan and Mercer, 1988; Frind et al., 1989; Kindred and Celia, 1989; Semprini and McCarty, 1991).

Some authors assume that, when diffusion mechanisms between the aqueous mobile phase and bacteria are dominant, sites of bacterial activity are localized in "microcolonies" of definite shape (Widdowson et al., 1988; Chen et al., 1992) or uniformly distributed in the porous medium (Taylor and Jaffé, 1990). In other cases, there is no assumption concerning the structure of the microbial community and the description of microbial activity is made from a macroscopic point of view (Kinzelbach and Schäfer, 1991; Lensing et al., 1994; Zysset et al., 1994). As pointed out by Baveye and Valocchi (1989), this kind of model is the most appropriate one when there is no clear experimental evidence of the structure of the bacterial community in an aquifer.

Recently, Lensing et al. (1994) presented such a model for transport and biodegradation in an aquifer including thermodynamic equilibrium modeling and four different species of bacteria. In this article, we present a conceptually similar, but simpler, model based on organic matter mineralization with emphasis on nitrogen species behavior (nitrate, ammonium). The aim of this model is to simulate the evolution of dissolved redox-sensitive species in the case of bank-filtration. The model is first tested with the column experiments by von Gunten and Zobrist (1993). A field application of the model to an experimental bank-filtration site in France is then described. The main character-

istics of the site are briefly reviewed. Finally, on the basis of a sensitivity analysis, some conclusions are drawn regarding the efficiency of bank-filtration in drinking water production.

2. Bank-filtration at the experimental study site in France

The site is located on an island which forms part of an important well field along the Seine river (France), 40 km downstream from Paris, with a daily production of ~ 150,000 m^3 of water. Note that at this point the Seine river is heavily influenced by effluents from the Achères sewage treatment plant. The aquifer consists of fissured Senonian chalk and ~ 10 m of alluvial deposits, i.e. from top to bottom, sandy clays, shelly sands and coarse alluvial deposits (Fig. 1). The hydrodynamic and hydrochemical characteristics of the site relevant to bank-filtration were studied with data gathered over one year (for details see Doussan et al., 1994; Poitevin, 1995). The water pumped in the
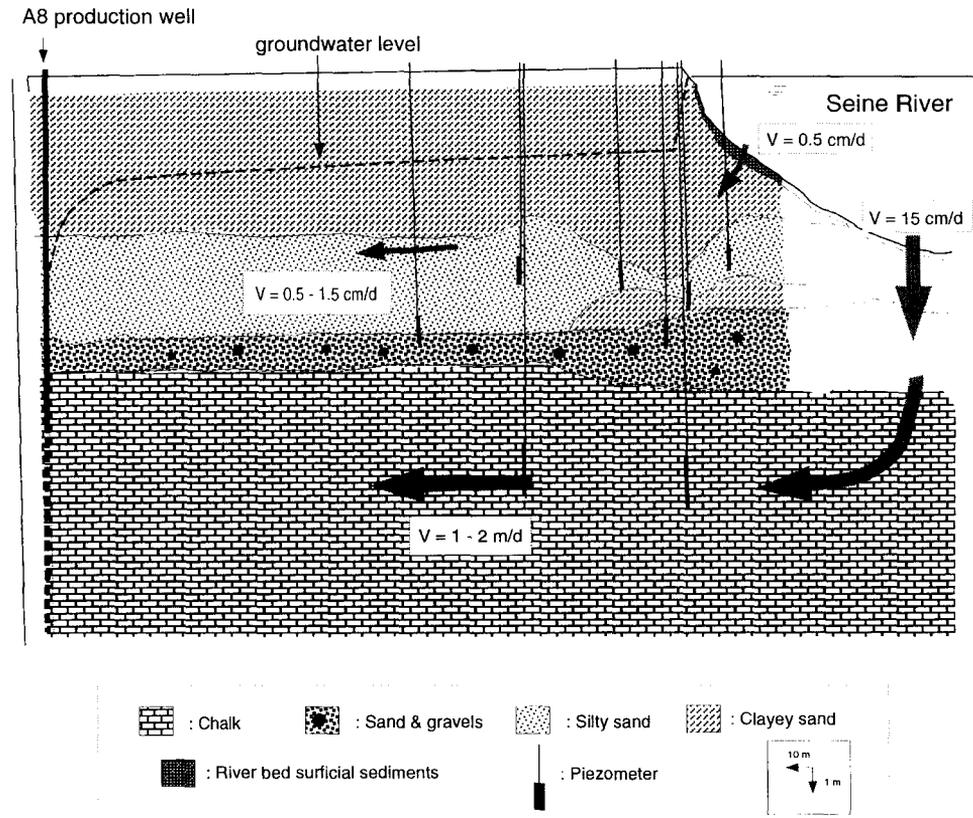

Fig. 1. Geological cross-section of the bank-filtration experimental site (Seine river, France) showing piezometer array and major hydrodynamic features.
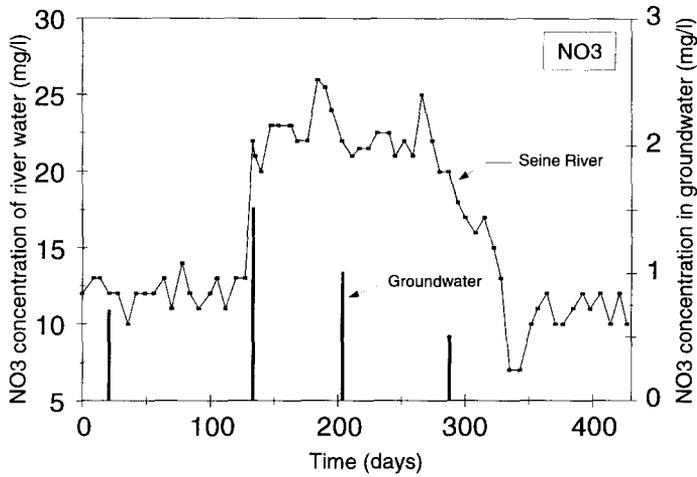
Fig. 2. Evolution of NO_3 concentrations in the Seine river and in a piezometer 5 m away from the bank (first piezometer in chalk near the river). Nitrate concentration in the aquifer is always below detection limit (0.5 mg/l) except on a few occasions shown in the figure. (3 July 1990 is the initial time in the figure.)
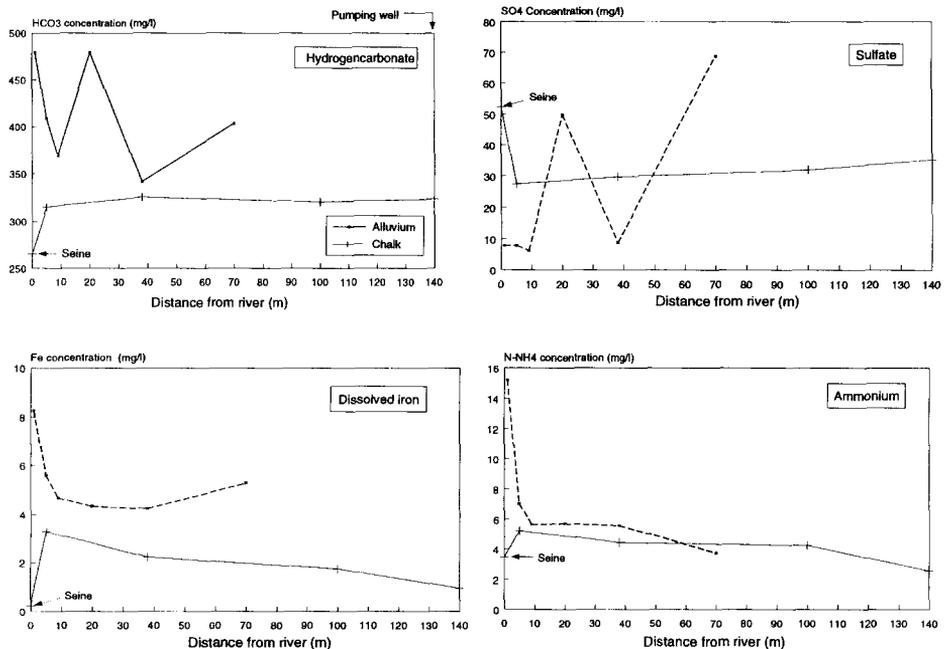

Fig. 3. Concentration profiles of dissolved Hydrogencarbonate, sulfate, iron, and ammonium along a flow path of the aquifer from the Seine river to pumping well A8.
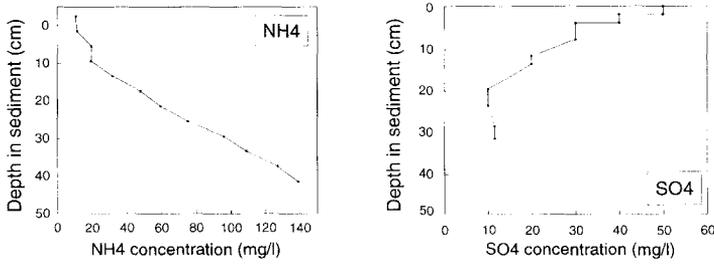
Fig. 4. Concentration profiles of sulfate and ammonium in the submerged Seine river bed sediments located close to the banks. Flux of infiltrating water is directed downward. Pore water was sampled by coring followed by centrifugation–filtration (Doussan, 1994).

well on the island (A8 well) comes almost exclusively from the Seine river. However, the chemical characteristics of the groundwater are very different from those of the river. This is due to highly reducing conditions, particularly near the banks. These conditions are stable over time in the whole aquifer. Thus, in contrast to the Seine river water, the nitrate, nitrite and oxygen have totally disappeared in the groundwater whereas sulfate concentration is halved (Figs. 2 and 3). However, ammonium, dissolved iron and manganese, hydrogen sulfur and hydrogencarbonate are found in the groundwater at much higher concentrations than in the river water. The concentration profiles in the aquifer show only small variations with distance to the river except near the banks (and at some locations in the alluvial deposits because of surficial infiltrations). In fact, most of the chemical changes in the water happen in the submerged superficial sediments of the river. Owing to the large quantity of solid organic matter in these sediments, bacterial mineralization is high and denitrification, sulfate reduction, as well as methano-genesis occur. At the same time, ammonium accumulates in the pore water of these river bed sediments due to the reducing environment (Fig. 4). An important point is that these changes are much less intense in the sediments in the middle of the river than in those near the banks (Figs. 4 and 5). Indeed, the sediments in the middle of the river show a greater flux of percolating water and a lower organic matter content than those close to the banks. This is reflected in the aquifer by the differences in groundwater chemistry between chalk and alluvial deposits.
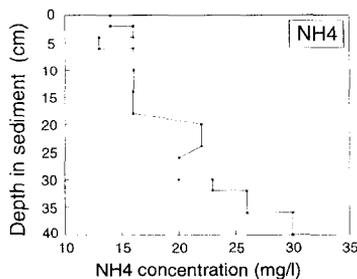

Fig. 5. Concentration profile of ammonium in the Seine river bed sediments located in mid-river. Flux of water is directed downward. Pore water was sampled by coring followed by centrifugation–filtration (Doussan, 1994).

3. Conceptual model of the biogeochemical evolution of infiltrating water

In line with the experimental evidence presented above, we consider that the major evolution of nitrogen species during river–groundwater transfer takes place in the first few meters of infiltration into the submerged river bed sediments. This evolution depends on carbon mineralization and bacterial activity. In this infiltration zone, the flow can be considered saturated and one-dimensional (Doussan, 1994). Fig. 6 shows a diagram of the evolution of the water chemistry between the river and the aquifer. Nutrients as electron acceptors (O_2, NO_3, etc.) are supplied by the infiltrating river water. Electron donors (organic matter) are supplied by the river water and the solid organic matter present in the sediments of the river (Fig. 7). Typically, electron acceptors are used by bacteria for energy purposes in a sequential order involving: O_2, NO_3, MnO_2,FeOOH, SO_4, CO_2, and some organic molecules for fermentative metabolism, in decreasing order of reaction energy (Stumm and Morgan, 1981). Thus, different layers can be distinguished in the sediment as one type of electron acceptor is consumed until exhausted. In the next layer down the next electron acceptor is used according to the above sequence. However, some overlapping of these layers is possible. For example, denitrification can occur even when oxygen is present (Bonin and Raymond, 1990) or methanogenesis can start although sulfates are present (Bouwer and Cobb, 1987). During mineralization of organic matter, various metabolites are excreted into the surrounding environment by bacterial catabolism, as is the case of phosphate and ammonium. The latter can be oxidized in the surficial oxygenated layers of sediment by nitrifying bacteria or transported deeper into the aquifer. An important point is that the solid organic matter cannot be used, as such, by microorganisms. Hydrolysis and solubilisation of these compounds are necessary steps for later energy or growth use. Hydrolysis of organic matter is done by extracellular enzymes which are produced by fermentative anaerobic bacteria (Desjardins and Lessard, 1992). Finally, from a physical point of view, it should be noted that some compounds (organic matter, ammonium) can be adsorbed on the solid phase. Moreover, the surficial layers of the river sediment are
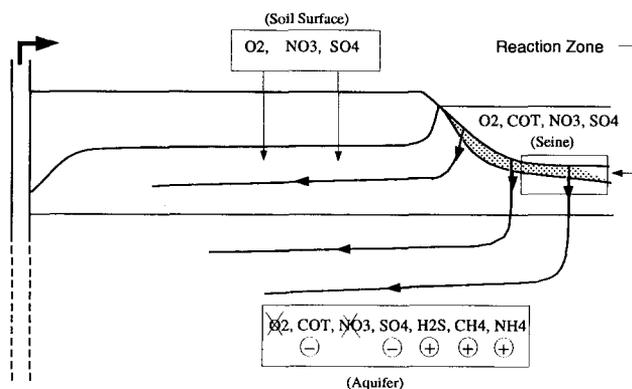

Fig. 6. Schematic evolution of water chemistry during transfer from the river to the aquifer. Signs $\times$, $\oplus$ and $\ominus$ respectively mean decrease below detection limit, increase and decrease of concentration during transfer.
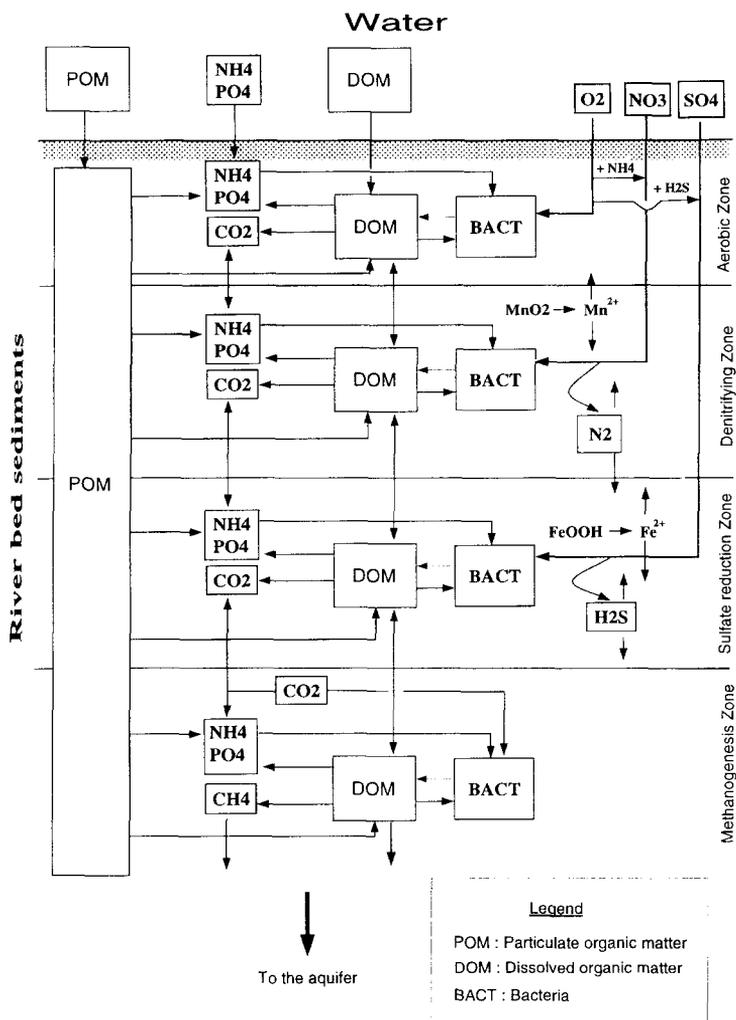
Fig. 7. Conceptual model of biogeochemical processes affecting chemical water characteristics during percolation through river bed sediments.

stirred up by benthic fauna (bioturbation), by the turbulent energy of the river and by fluvial navigation. This enables nutrients to penetrate more deeply into the river bed sediments.

4. Model development

4.1. Species

In order to describe the evolution of nitrogen species, we need to include nitrate and ammonium. The latter is heavily dependent on the mineralization which occurs with

different electron acceptors (O_2, NO_3, etc.). Therefore, in order to evaluate the redox state of the filtrate, we consider the different electron acceptors (e.g., O_2, NO_3, SO_4) together with organic matter (solid and dissolved) and CH_4 for the methanogenesis. Organic matter is divided into two biodegradability classes to account for the varying ability of bacteria to degrade organic molecules (Billen et al., 1989). Iron and manganese are not considered here, although their solid hydroxide forms may be used as energy sources by bacteria (Lovley, 1991). They have a much more complicated chemical behavior, which depends on the redox state and the pH of the water and needs chemical equilibrium modelling (Lensing et al., 1994).

4.2. Bacterial activity

The growth of bacteria is greatly affected by a number of environmental parameters: temperature, nutrients, pH, toxic elements, interactions with other organisms, etc. However, it is difficult to explicitly account for all these factors and their interactions. As a result, models of microbial growth are generally based on some limiting environmental factors and bacteria concentration. Here, we used an extended form of the classical Michaelis–Menten equation, which assumes that nutrients are the limiting factors of the growth rate:

$$\mu = \mu_{max} \frac{S_1}{K_{S_1} + S_1} \frac{S_2}{K_{S_2} + S_2} \tag{1}$$

where μ is the specific growth rate; S_1 and S_2 are limiting substrate concentrations which are, typically, a mineral electron acceptor and an organic electron donor; μ_{max} is the maximum specific growth rate and K_{S_i} is the Michaelis constant (or substrate half-saturation constant).

The effect of the temperature, which fluctuates strongly in the river, is incorporated in the maximum specific growth rate via a power law:

$$\mu_{max}(T) = \mu_{max}(20) \cdot \theta^{(T-20)} \tag{2}$$

where the reference temperature is 20°C; and θ is the parameter describing the temperature influence on maximum specific growth rate.

The bacteria in the sediment are assumed to live closely together and to be capable of very diverse metabolic activity. In particular, the different types of mineralization considered here are effective everywhere in the sediment if the inhibition by electron acceptors of higher redox levels is suppressed. With these assumptions, only one bacterial population is considered. There are three reasons for this choice: (1) some bacteria are optional aerobes (e.g., aerobic respiration–denitrification); (2) surficial layers of sediment are mixed by turbulent energy of the river water; and (3) the bacteria can move in the pore water toward higher concentrations of nutrients (chemiotactism).

The general method for modelling uptake inhibition is based on the definition of an inhibition factor. It is defined as:

$$I(A) = 1 + \frac{A}{K_A} \tag{3}$$

where A is the concentration of the different inhibiting substances (O_2, NO_3, SO_4); and K_A is the inhibition constant. Here, we used noncompetitive inhibition which means that the inhibiting substance acts as if all functioning enzymes of the bacteria are reduced by the inhibitor. In this case, the maximum specific growth rate (μ_{max}) is divided by $I(A)$ (Kindred and Celia, 1989). Consequently, if A is much smaller than K_A, then $I(A)$ is close to 1 and there is almost no inhibitory effect and inversely, if A is much greater than K_A, the inhibitory effect may be quite strong.

The rate of bacterial development is given by the following expression:

$$R_\rho = \sum_i \mu_i \, \rho - b\rho \tag{4}$$

where ρ is the concentration of the microorganisms, expressed in terms of carbon concentration; μ_i is the specific growth rate for the different kinds of respiration (aerobic respiration, nitrate and sulfate reduction, methanogenesis); and b is the decay rate constant of microorganisms.

The complete mathematical formulation for rates of consumption or production of dissolved electron acceptors, electron donors is presented in Fig. 8.

Bacterial activity also acts on dissolution of solid organic matter (SOC) through the action of hydrolytic exoenzymes. This supplies the bacteria with biodegradable dissolved organic matter (DOC) of low molecular weight. It is represented by a second-order reaction term:

$$R_{sol} = k_{sol} \, SOC \, \rho \tag{5}$$

where k_{sol} is the second–order solubilisation rate constant.

As mentioned above, most of the bacteria are located on the solid phase; we therefore neglect the activity of bacteria in the liquid phase. Mobility of bacteria in the pore water is considered as a mean of colonizing new sites in the sediment when conditions become favorable to their specific metabolic activity.

4.3. Coupling with transport

Because the biofilm develops on the solid phase of the porous medium, the transport model should include multiple-phase kinetics. We therefore describe mass transport in the mobile aqueous phase and diffusion-limited exchange in the immobile water-biomass phase. This diffusion limitation is assumed to be governed by a capacitance-like relation with no assumption on the spatial arrangement of the microbial population. As pointed out by Kinzelbach and Schäfer (1991), this kinetic limitation may be viewed as a microscale diffusion (in the biofilm) or as a macroscale exchange between different zones of the porous medium.

The macroscopic unidimensional mass-balance equation can be written for the two phases:

(a) Mobile phase:

$$\omega_m \, R_{rx} \frac{\partial X_m}{\partial t} = D \frac{\partial^2 X_m}{\partial z^2} - U \frac{\partial X_m}{\partial z} - \gamma (X_m - X_{im}) \tag{6}$$

(b) Immobile phase:

$$\gamma(X_m - X_{im}) = R_X \tag{7}$$

where X_m and X_{im} are the concentrations of component X in the mobile and immobile phase, respectively; ω_m is the macroscopic volumetric fraction of the mobile phase; D is the dispersion coefficient; U is the Darcy velocity; R_{rx} is a retardation factor; γ the interphase transfer coefficient; and R_X is the source/sink term of microbial activity (see Fig. 8). In these equations, it is assumed that the immobile water phase is at steady state with respect to concentrations (i.e. the rate of change of solute mass in the immobile phase is much smaller than that in the mobile phase) and that ω_m stays constant (effects on porosity of microbial growth are neglected). The transport equation with source/sink terms for the different species is given in Fig. 9.

• **Oxygen** : $R_O = R_O^1 + R_O^2 + R_{Nit}$ (aerobic respiration + nitrification)

$$R_O^1 + R_O^2 = (1 - Y_0)\,\beta_0 \sum_{i=1}^{2} \left(\frac{\mu_O^i}{Y_0} \frac{DOC^i}{K_{CO}^i + DOC^i} \frac{O}{K_O + O}\rho \right) \qquad \text{Aerobic respiration}$$

$$R_{Nit} = \mu_{Ni} \frac{NH_4}{K_{Ni} + NH_4} \frac{O}{K_{ON} + O} \qquad\qquad\qquad \text{Nitrification}$$

• **Nitrate** : $R_{NO_3} = R_{NO_3}^1 + R_{NO_3}^2 - \lambda_{NO_3} R_{Nit}$ (denitrification + nitrification)

$$R_{NO_3}^1 + R_{NO_3}^2 = (1 - Y_N)\,\beta_N \sum_{i=1}^{2} \left(\frac{\mu_N^i}{Y_N} \frac{DOC^i}{K_{CN}^i + DOC^i} \frac{NO_3}{K_N + NO_3}\rho \right) \times \left(1 + \frac{O}{K_{ON}} \right)^{-1}$$

• **Sulfate** : $R_{SO_4} = R_{SO_4}^1 + R_{SO_4}^2$ (sulfate reduction)

$$R_{SO_4}^1 + R_{SO_4}^2 = (1 - Y_S)\,\beta_S \sum_{i=1}^{2} \left(\frac{\mu_S^i}{Y_S} \frac{DOC^i}{K_{CS}^i + DOC^i} \frac{SO_4}{K_S + SO_4}\rho \right) \times \left(1 + \frac{NO_3}{K_{NS}} \right)^{-1} \left(1 + \frac{O}{K_{OS}} \right)^{-1}$$

• **Methanogenesis** : $R_{CH_4} = R_{CH_4}^1 + R_{CH_4}^2$

$$R_{CH_4}^1 + R_{CH_4}^2 = (1 - Y_{CH_4})\,\beta_{CH_4} \sum_{i=1}^{2} \left(\frac{\mu_C^i DOC^i}{Y_{CH_4}}\rho \right) \times \left(1 + \frac{SO_4}{K_{SC}} \right)^{-1} \left(1 + \frac{O}{K_{OS}} \right)^{-1}$$

• **Dissolved Organic Carbon** : R_{DOC}

$$i = 1,2 \qquad R_{DOC}^i = \frac{R_0^i}{(1 - Y_2)\beta_0} + \frac{R_{NO_3}^i}{(1 - Y_N)\beta_N} + \frac{R_{SO_4}^i}{(1 - Y_S)\beta_S} + \frac{R_{CH_4}^i}{(1 - Y_{CH_4})\beta_{CH_4}}$$

• **Ammonium** : R_{NH_4}

$$R_{NH_4} = \sum_{i=1}^{2} \lambda_{Ni} \left(\frac{R_O^i}{\beta_O} + \frac{R_{NO_3}^i}{\beta_N} + \frac{R_{SO_4}^i}{\beta_{SO_4}} + \frac{R_{CH_4}^i}{\beta_{CH_4}} \right) - \lambda_{NO_3} R_{Nit}$$

* superscripts 1,2 and i (=1,2) stand for two types of organic matter differing in bioavaibility for bacteria.

Fig. 8. Source/sink terms of microbial processes considered in the model.c

Liquid phase[*]

- **Oxygen** :

$$\frac{\partial O_m}{\partial t} = L(O_m) - \frac{\gamma}{\omega_m}(O_m - O_{im})$$

$$\gamma(O_m - O_{im}) = R_O$$

- **Nitrate** :

$$\frac{\partial NO_{3_m}}{\partial t} = L(NO_{3_m}) - \frac{\gamma}{\omega_m}(NO_{3_m} - NO_{3_{im}})$$

$$\gamma(NO_{3_m} - NO_{3_{im}}) = R_{NO_3}$$

- **Sulfate** :

$$\frac{\partial SO_{4_m}}{\partial t} = L(SO_{4_m}) - \frac{\gamma}{\omega_m}(SO_{4_m} - SO_{4_{im}})$$

$$\gamma(SO_{4_m} - SO_{4_{im}}) = R_{SO_4}$$

- **Methanogenesis** :

$$\frac{\partial CH_{4_m}}{\partial t} = L(CH_{4_m}) - \frac{\gamma}{\omega_m}(CH_{4_m} - CH_{4_{im}})$$

$$\gamma(CH_{4_m} - CH_{4_{im}}) = R_{CH_4}$$

- **Dissolved organic carbon** :

$$i = 1, 2 \qquad \frac{\partial DOC_m^i}{\partial t} = L(DOC_m^i) - \frac{\gamma}{\omega_m}(DOC_m^i - DOC_{im}^i)$$

$$\gamma(DOC_m^i - DOC_{im}^i) = R_{DOC}^i + R_{sol}^i + R_{sat}^i$$

$$R_{sat}^i = \alpha(C_{sat} - DOC_{im}^i)$$

- **Ammonium** :

$$\frac{\partial NH_{4_m}}{\partial t} = L(NH_{4_m}) - \frac{\gamma}{\omega_m}(NH_{4_m} - NH_{4_{im}})$$

$$\gamma(NH_{4_m} - NH_{4_{im}}) = R_{NH_4}$$

Solid phase

- **Solid organic carbon** :

$$\frac{\partial SOC}{\partial t} = D_s \frac{\partial^2 SOC}{\partial z^2} - R_{sol}^i - R_{SAT}^i$$

- **Bacteria** :

$$\frac{\partial \rho}{\partial t} = D_s \frac{\partial^2 \rho}{\partial z^2} + \sum_{i=1}^{2} \left(\frac{Y_O R_O^i}{(1 - Y_O)\beta_0} + \frac{Y_N R_{NO_3}^i}{(1 - Y_N)\beta_N} + \frac{Y_S R_{SO_4}^i}{(1 - Y_S)\beta_S} + \frac{Y_C R_{CH_4}^i}{(1 - Y_C)\beta_C} \right) - b\rho$$

[*] $L(X) = \frac{D}{\omega_m}\frac{\partial^2 X}{\partial z^2} - \frac{U}{\omega_m}\frac{\partial X}{\partial z}$ – *m: mobile phase, im: immobile phase*

Fig. 9. System of transport equations including source/sink terms for the species considered.

Adsorption is considered only for ammonium, through the retardation factor which includes effects of a linear adsorption isotherm, and for organic carbon via a source/sink term similar to a capacitance-like relation (Kinzelbach and Schäfer, 1991; Fig. 9).

As there is mixing of the solid phase, there are also two mass-balance equations for solid organic matter and bacteria adhering to the solid matrix (Fig. 9).

4.4. Numerical solution

The general system of partial differential equations developed here can be summarized schematically by equations of the form:

$$\frac{\partial X_i}{\partial t} = D \frac{\partial^2 X_i}{\partial z^2} - u \frac{\partial X_i}{\partial z} + S(X_1, \ldots, X_i, \ldots, X_n) \tag{8}$$

where $S(X_1, \ldots, X_i, \ldots, X_n)$ is the nonlinear source/sink coupling term.

This system is solved with an operator splitting scheme (Noye, 1987; Engesgaard and Kipp, 1992) in which the term $(\partial X_i / \partial t)$ is split into a pure transport component:

$$\left(\frac{\partial X_i}{\partial t} \right)_{\text{transp}} = D \frac{\partial^2 X_i}{\partial z^2} - U \frac{\partial X_i}{\partial z} \tag{9}$$

and a reaction component

$$\left(\frac{\partial X_i}{\partial t} \right)_{\text{reac}} = S(X_1, \ldots, X_i, \ldots, X_n) \tag{10}$$

This leads to a linear transport subproblem and a set of ordinary differential equations for the reactions. The transport subproblem is solved by an implicit finite-difference method. In order to limit the numerical dispersion and to avoid stability problems the advective term $(\partial X / \partial z)$ is approximated by a four-node formulation (Leonard, 1979):

$$\frac{\partial X}{\partial z} = \frac{2 X_{i+1} + 3 X_i - 6 X_{i-1} + X_{i-2}}{6 \, \mathrm{d} z} \tag{11}$$

The dispersive term is discretized by a central finite-difference scheme.

The numerical solution of the reaction component, which leads to a set of nonlinear equations after an implicit discretisation, is achieved with an iterative Newton–Raphson–Kantarovich quasi-linearization method (Molz et al., 1986). Indeed, for each compound X_i we have a nonlinear equation $f_i(X_1, \ldots, X_i, \ldots, X_n)$ which is approximated by:

$$X_i^{(m+1)} = X_i^{(m)} - \frac{f_i\left(X_1^{(m)}, \ldots X_i^{(m)}, \ldots X_m^{(m)}\right)}{f_i'\left(X_1^{(m)}, \ldots X_i^{(m)}, \ldots X_m^{(m)}\right)} \tag{12}$$

in which m is an iteration index; and f_i' is the first derivative of f_i with respect to X_i.

A new approximation of X_{i+1} is therefore calculated with the updated value of X_i. The concentrations of each species are serially updated for each node and the iterative procedure continues until the concentrations become constant at each node subjected to a predetermined tolerance criterion. Generally, just a few iterations are needed to achieve convergence.
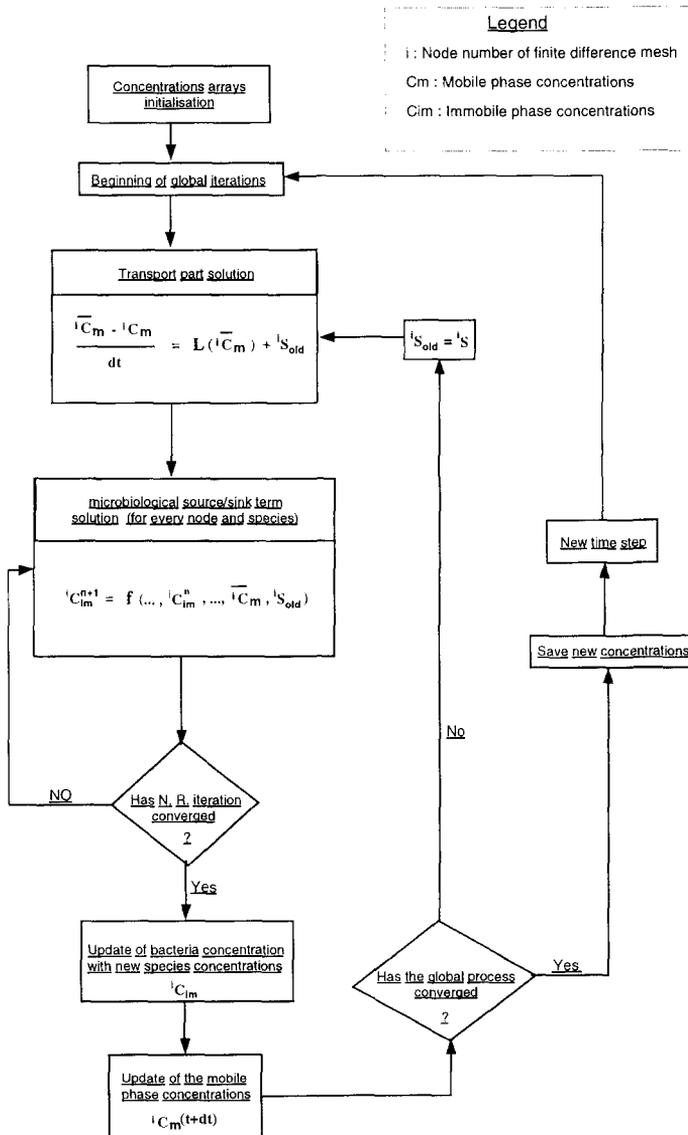
Fig. 10. Flow chart of the iterative numerical scheme.

The solution of the global system of nonlinear partial differential equations is found by iteration as shown in Fig. 10. In a first half-step, the transport component is solved with the source/sink reaction term of the preceding iteration explicitly incorporated. In a second half-step, the source/sink reaction term and concentrations of the reaction step are calculated with the solution to the transport component as initial condition. The system is iterated until convergence of concentrations is obtained. The time step must be

small enough to minimize the number of numerical errors associated with the operator splitting scheme (Valocchi and Malmstead, 1992). In order to insure convergence the Courant number should be smaller than 1.

The boundary conditions used here are: imposed concentrations at the inlet of the sediment column (river concentrations of the different species) and a zero gradient condition at the outlet. As initial condition we need the concentration profiles in the sediment of the species considered as well as profiles of bacteria and solid organic carbon.

5. Results and discussions

5.1. Simulation of column experiments

To test the consistency of the transport model with the biological interactions described above, we applied it to the column experiments by von Gunten and Zobrist (1993) whose data have also been used by Zysset et al. (1994) for model testing. These experiments are of interest mainly because they were designed to simulate infiltration of an organically polluted river into an aquifer. Thus synthetic river water including an organic substrate (lactate) and mineral electron acceptors was injected at a constant rate, into columns filled with river sediments. In the first small column (column a), only nitrate is added to the solution as an electron acceptor. In the second column (column b), oxygen, nitrate and sulfate are used as electron acceptors. Samples of the percolating water were taken along the columns by means of sampling ports. The experiments were started by inoculating the water in the columns with a small amount of bacteria. As a result of these experiments, von Gunten and Zobrist (1993) observed the redox sequence of dissolved electron acceptors and confirmed that Fe- and Mn-hydroxides also act as solid electron acceptors. In the following simulations, the latter are not included; we studied coupled transport of O_2, NO_3 and SO_4. According to Zysset et al. (1994), the dispersivity and the porosity are the same for both columns. Apart from the difference in the electron acceptor compositions of the water, the two columns have different injection flow rates (1.83 m day^{-1} in column a, and 0.37 m day^{-1} for column b). The results of the nitrate simulation for column a are assumed to be applicable to column b because the sediment material is the same in both cases. The simulations discussed here deal with transient nitrate evolution in columns a and b, and coupled transient transfer and evolution of oxygen, nitrate and sulfate in column b.

5.1.1. Denitrification

According to the authors cited above, the major reaction affecting nitrate behavior in both columns is denitrification. Nitrate is reduced to $N_{2(g)}$, while organic substrate (lactate) is oxidised. These experiments also show that nitrate, rather than lactate $(C_3H_5O_3^-)$ is the limiting nutrient for bacterial growth. The nitrate reduction with lactate is:
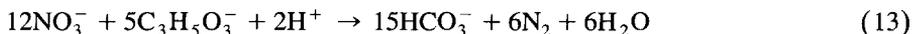
$$12NO_3^- + 5C_3H_5O_3^- + 2H^+ \rightarrow 15HCO_3^- + 6N_2 + 6H_2O \tag{13}$$

Table 1
Physical parameters and boundary conditions used in the simulation of column experiments

	Column a	Column b
Darcy velocity (m/day)	1.8	0.37
Dispersivity (m)	0.001	0.001
Porosity	0.4	0.4
Kinematic porosity	0.37	0.37
O_2 for $x = 0$ (mg/l O_2)	–	7
NO_3 for $x = 0$ (mg/l NO_3)	34.1	18.6
SO_4 for $x = 0$ (mg/l SO_4)	–	22.1-20.9
DOC for $x = 0$ (mg/l C)	43.2	43.2

from which we obtain the stoichiometric coefficient $\beta_N = 4.13$ mg NO_3/mg C which is used in the simulation. According to Zysset et al. (1994), the yield coefficient (Y_N) ranges between 0.3 and 0.5. The value of Y_N used here is 0.4. The half-saturation constant for simple substrates such as lactate is in the range of a few mg/l (Roques, 1979; Marty et al., 1989). We used a value of 3 mg/l, since lactate is not limiting (lactate input concentration: 43 mg/l C).

Lactate is taken to be the only organic substrate used by the bacteria. Indeed, the sediment used in these experiments (sand) has little solid organic carbon ($< 0.1\%$). Thus, solid organic matter dissolution is not included in the simulation. The decay constant of the bacterial population is 0.05 day^{-1} according to Zysset et al. (1994). Boundary conditions and hydrodynamic parameters are given in Table 1.

With the available information three parameters have to be calibrated: the interphase transfer coefficient (γ) and the biochemical parameters of denitrification: maximum specific growth rate (μ_{max}) and half-saturation constant (K_N). These parameters are also used for the column b simulation.
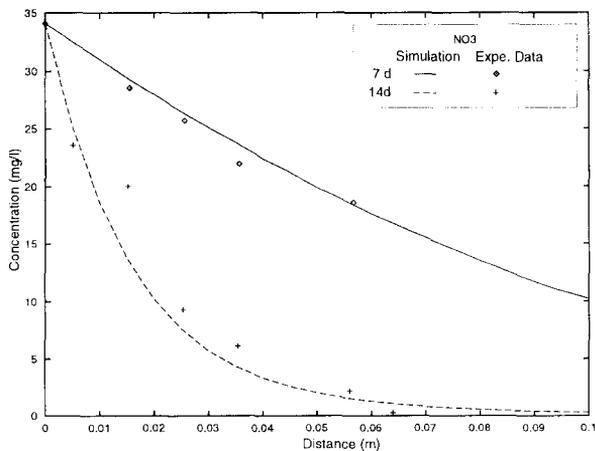

Fig. 11. Simulated (*lines*) and observed (*points*) nitrate concentration profiles in column a, 7 and 14 days after start of experiment.

Table 2
Microbiological parameters used in the simulation of column experiments

	O_2	NO_3	SO_4
Maximum specific growth rate constant, μ_{max} (day^{-1})	10	1.44	0.26
Half-saturation constant of electron acceptors (mg/l)	0.77	7	5.35
Half-saturation constant of electron donor (mg/l)	3	3	3
Microbial yield (mg microbial carbon/mg DOC)	0.5	0.4	0.4

	$O_2 \rightarrow NO_3$	$O_2, NO_3 \rightarrow SO_4$
Inhibition constants (mg/l)	10^{-3}	$2 \cdot 10^{-3}$

Results of the column a simulation are presented in Fig. 11 and show that the experimental results can be fitted by the model. Table 2 gives the calibrated parameters.

To simulate the nitrate evolution in column b, most of the parameters can be taken from the column-a experiment, especially the calibrated parameters since the two experiments differ only in flow velocity and concentration of the inflowing compounds. However, oxygen and sulfate also act as electron acceptors in this case. Bacterial parameters of oxygen utilization (Table 2) are from Molz et al. (1986), and Bouwer and Cobb (1987). The inhibition constant of oxygen on denitrification has to be calibrated. A comparison between the calculated and experimental data for steady state is shown in Fig. 12. The steepest fall of nitrate concentration over a distance in the centimeter range is well reproduced by the model with a small overestimate of nitrate concentration. This deviation is not large but may show some dependence by the interphase transfer coefficient (γ) on flow velocity. It is worth noting that simulated oxygen profiles are coherent with the results of von Gunten and Zobrist (1993) who show that oxygen
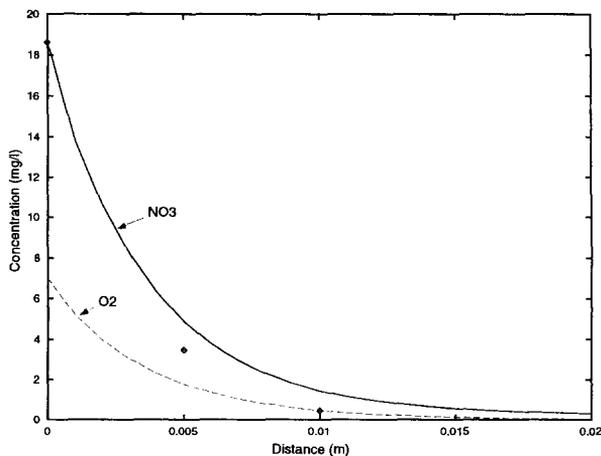

Fig. 12. Simulated (*lines*) and observed (*points*) nitrate concentration profiles in column b for steady state. Simulated oxygen profile is also shown.
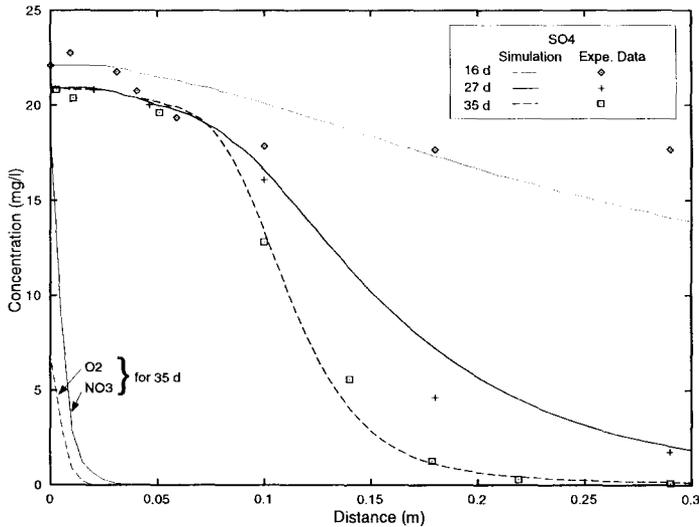
Fig. 13. Sulfate concentration profiles simulated (*lines*) and observed (*points*) in column b. Simulated oxygen and nitrate profiles are also shown for 35 days after start of experiment.

concentration falls by 0.1 mg/l after 1.8 cm. The model seems to show a relatively good fit for the two experiments of coupled nitrate and oxygen transfer.

5.1.2. Sulfate reduction

The transient evolution of sulfate in column b was simulated together with that of oxygen and nitrate. In this column, organic matter is successively oxidised by oxygen, nitrate and sulfate. Denitrification is inhibited by oxygen while sulfate reduction is inhibited both by oxygen (oxygen is toxic for sulfate-reducing bacteria) and nitrate. This oxygen inhibition may be seen on data by von Gunten and Zobrist (1993; Fig. 13) where there is almost no sulfate reduction in the first 5 cm of column b.

According to Zysset et al. (1994), sulfate reduction can be represented as follows:

$$3\,SO_4^{2-} + 4\,C_3H_5O_2^- \rightarrow 3\,HS^- + 4\,C_2H_3O_2^- + 4\,HCO_3^- + H^+ \qquad (14)$$
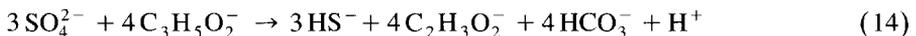
with a stoichiometric coefficient $\beta_S = 6$ mg SO_4/mg C. Like Zysset et al. (1994), we suppose that the yield coefficient of sulfate reduction is the same as that of nitrate reduction ($Y_S = 0.4$). Oxygen and nitrate parameters are the same as those used in the denitrification simulation as well as for the decay rate constant and half-saturation of organic substrate (Table 2). Bacterial parameters of the sulfate reduction (specific maximum growth rate and half-saturation constant) and the inhibition constant are calibrated. Experimental and simulated data are presented in Fig. 13 and the parameters are listed in Table 2.

Transient sulfate evolution is well represented by the model, except in early time of sulfate reduction (which takes place after $\sim$ 16 days) at the end of the column. This may be attributed to an approximate representation in the model input of the initial bacterial distribution along the column linked to the inoculation procedure.

Thus, the model can reasonably well represent experimental results of simultaneous coupled utilization by bacteria of oxygen, nitrate and sulfate with an organic substrate in column experiments. In particular, the influence on the steady-state concentration profiles of the change in hydrodynamic regime between columns a and b is quantitatively described by the model.

It is important to notice that, in these experiments, solid organic matter has no effect because it is nearly absent from the sediment. Growth of bacteria depends solely on the permanent influx of a compound easily biodegradable in percolating water. This is not the case at our experimental bank-filtration site. At this site, there is an important supply of solid organic matter which has a major influence on the biogeochemical characteristics of the bank-filtration phenomena. By applying the model to the characteristics of the experimental site, we obtain an example of the role of solid organic carbon in river bed sediments.

5.2. Applying the model to the experimental site

We now examine if the model can give results coherent with observations made on the river sediments of the experimental site (concentration profiles), and reproduce the features of the bank-filtration effect on the studied compounds. To this end, some parameters are estimated from laboratory experiments (Poitevin, 1995), from site measurements (Doussan, 1994) or from literature. The flux of percolating water in river bed sediments is constant throughout the simulation period. Model parameters are listed in Tables 3 and 4. Inhibition constants have been calibrated.

The simulation was run over a 6-month period and the result is shown in Fig. 14. The model can qualitatively reproduce the on-site findings: oxygen, nitrate and sulfate are gradually consumed whereas ammonium is accumulated in the sediment column. This ammonium production is the result of the strong mineralization of organic matter in the sediments. From a quantitative point of view, the depth of the nitrate penetration into the sediment is a little overestimated by the model (~ 5 cm, compared to 1–3 cm on the site), but that of sulfate penetration is somewhat underestimated. For ammonium, a rather good approximation of concentrations at depth is obtained, except for the highest

Table 3

Physical parameters and boundary conditions used in the simulation of concentration profiles in river bed sediments of the experimental site

Porosity	0.6
Darcy velocity (m/day)	$4 \cdot 10^{-3}$
γ (day^{-1})	10
Ammonium linear adsorption coefficient (m^3/kg)	$2 \cdot 10^{-3}$
O_2 for $x = 0$ (mg/l)	7
NO_3 for $x = 0$ (mg/l)	15
SO_4 for $x = 0$ (mg/l)	52
NH_4 for $x = 0$ (mg/l)	4.4
DOC for $x = 0$ (mg/l)	6.2
SOC (g/g)	0.01

Table 4

Microbiological parameters used in the simulation of concentration profiles in river bed sediments of the experimental site

	O_2	NO_3	SO_4	Methanogenesis
Maximum specific growth rate (day^{-1})	10	10	5	$8 \cdot 10^{-4}$
Half-saturation constant of electron acceptors (mg/l)	0.77	65	1	–
Half-saturation constant of electron donor (mg/l)	15	20	20	–
Yield coefficient (mg microbial carbon/mg DOC)	0.5	0.4	0.1	0.03
Decay rate constant (day^{-1})		$5 \cdot 10^{-3}$		
k_{sol} (l mg^{-1} day^{-1} C)		$4 \cdot 10^{-5}$		

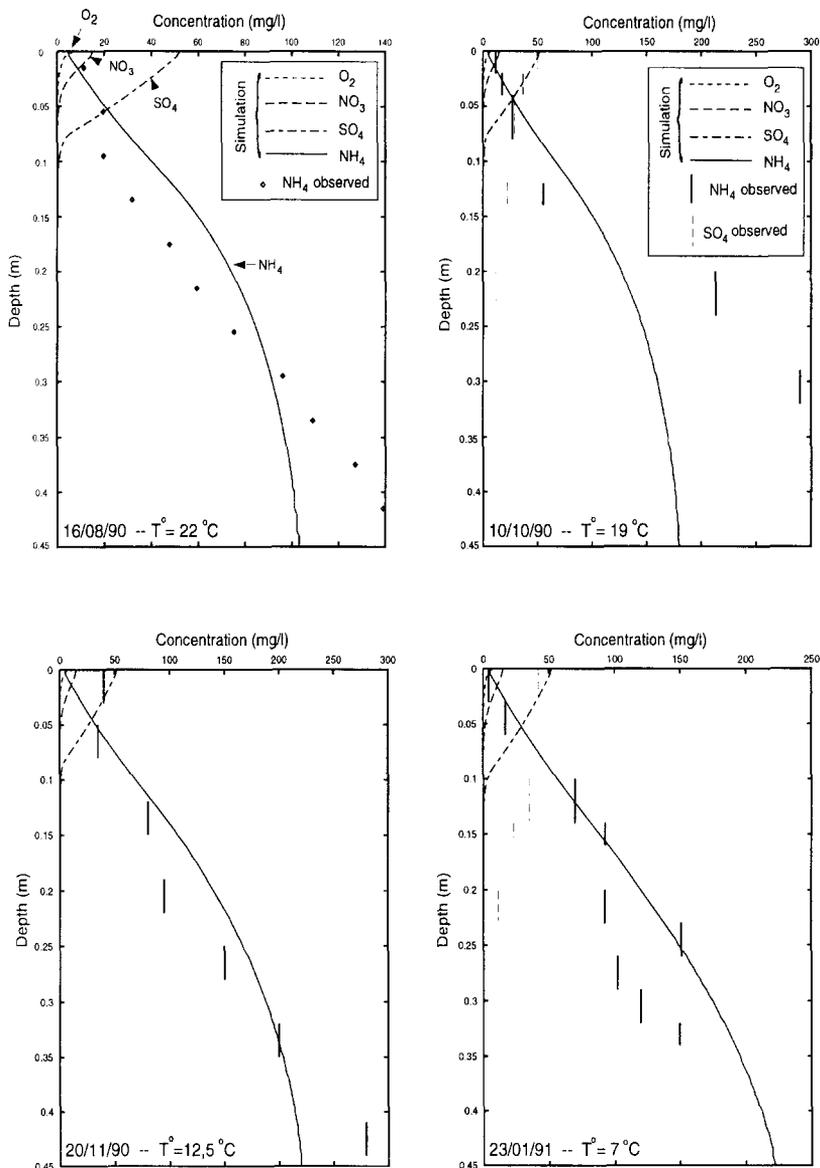|	$O_2 \rightarrow NO_3$	$NO_3 \rightarrow SO_4$	$SO_4 \rightarrow CH_4$	$O_2 \rightarrow SO_4, CH_4$
Inhibition constants (mg/l)	10^{-3}	$5 \cdot 10^{-4}$	$8 \cdot 10^{-4}$	$5 \cdot 10^{-5}$

Fig. 14. Concentration profiles of O_2, NO_3, SO_4 and NH_4 simulated for the period between August 1990 and January 1991 in the river bed sediments of the experimental site. Concentration profiles of ammonium and sulfate measured in core samples are also shown. Measured nitrate concentrations are always below analytical detection limit below 3-cm depth.

concentrations found in reality. Some of the discrepancies may be due to spatial variability in the distribution of parameters such as initial bacterial population or of organic matter vs. depth, which are considered constant in the model.

5.3. Some consequences for bank-filtration efficiency

This model may help to clarify which parameters are important for bank-filtration efficiency or behavior, especially in the case of nitrogen species. Sensitivity analyses were conducted with parameters taken from the experimental site simulation. For the purpose of comparison, the reference simulation is the one for the month of August on the experimental site (Fig. 14). In fact, two parameters are of major importance for the evolution of the chemistry of the percolating water: the pore-water velocity and the solid organic matter solubilisation.

The influence of pore-water velocity is shown in Figs. 15 and 16. The parameters in the simulation are the same as those used for the modelling of the experimental site with the exception of the pore-water velocity. The electron acceptors (particularly nitrate) penetrate deeper into the sediment. For example, with a pore-water velocity of 5 cm/day the penetration depth of nitrate is 10 cm, whereas with a pore-water velocity of 1 m/day this depth is ~ 0.7 m. Clearly, an increase in pore-water velocity decreases the extent of the anaerobic zone of organic matter mineralization and, consequently, lowers ammonium production and concentration.

The extreme case of zero solubilisation of solid organic matter is shown in Fig. 17. Here, bacteria can feed only on dissolved organic carbon in the river water percolating through the sediments. In this case, the results change drastically. Sulfate reduction and methanogenesis do not occur at all along the sediment column, and the relatively small input of organic matter from the river water to the system prevents ammonium formation and accumulation.
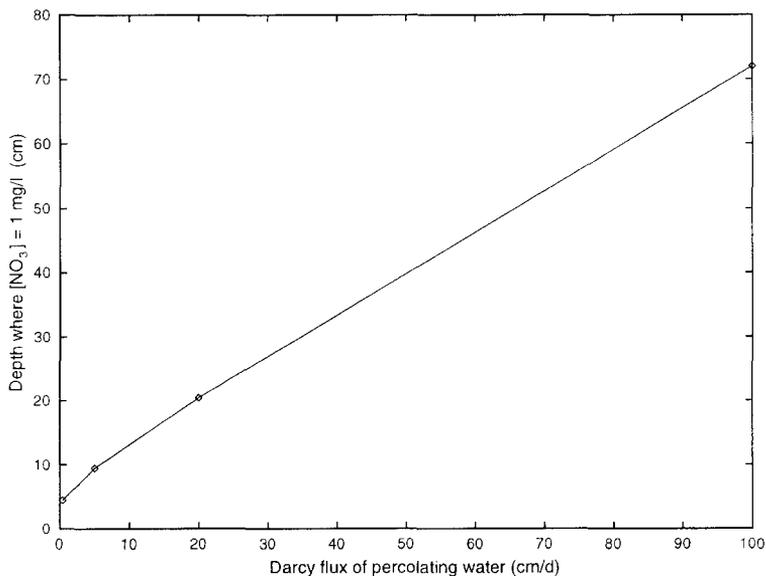

Fig. 15. Simulated relationship between penetration depth of nitrate (depth where $[NO_3] = 1$ mg/l) and Darcy velocity of percolating water.
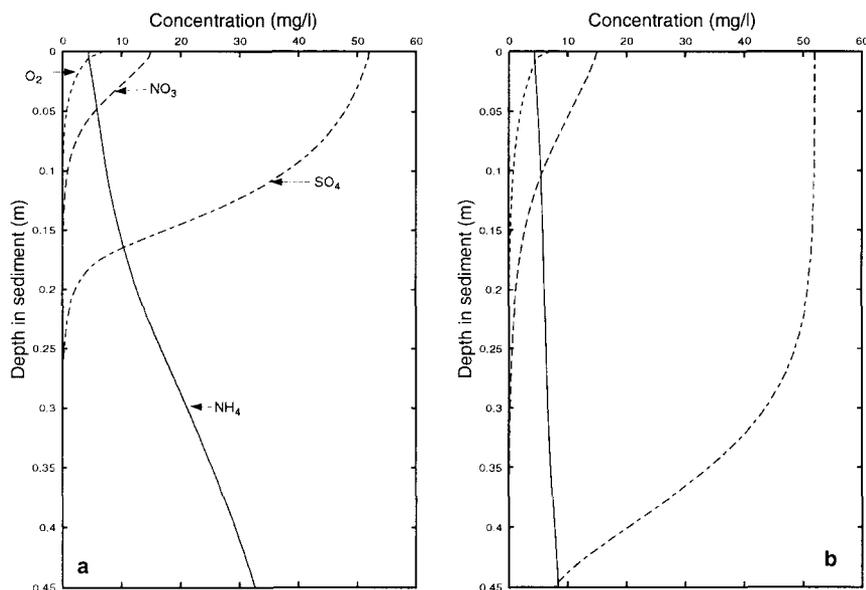
Fig. 16. Simuation of pore-water velocity influence on concentration profiles in sediments for: (a) 5-cm/day Darcy velocity; and (b) 20-cm/day Darcy velocity.

In a global vision of bank-filtration, given that necessary bacteria are present in the sediment, the flow rate of infiltrated water and supply of organic matter may crucially influence the chemical evolution of water, particularly with respect to the behavior of nitrogen species. When water velocity increases, it allows electron acceptors to penetrate more deeply in the sediment, which attenuates the reducing conditions (a side effect is that less ammonium is produced). It seems also that when river sediments contain $> 1\%$ of solid organic carbon, denitrification proceeds rapidly and reducing conditions may become established. This denitrification may become permanent if the sedimentary organic carbon is continuously renewed by sedimentation in the river and surficial mixing of the sediment layers. Paradoxically, input of organic carbon in the water course may therefore have a beneficial effect on nitrate elimination during bank-filtration and thus on water production. Wells located near the river and producing water made nitrate-free by bank-filtration may therefore have a considerable influence on the overall quality of the water supplied by alluvial well fields often threatened by agricultural nitrate. However, if the input of organic matter is too high, highly reducing conditions may become established in the aquifer and adversely affect the quality of the bank-filtrated water (ammonium production, iron and manganese dissolution). The quality of water pumped in a well near a river depends on subtle equilibria governed by pore-water velocity and amounts of available organic carbon in the first meters of river sediments. Consequently, it seems that a flux of water on the order of a few meters per day, combined with amounts of organic carbon in the sediments of $< 1–2\%$ should result in a high rate of denitrification without the drawbacks of severe reducing conditions and significant ammonium production.
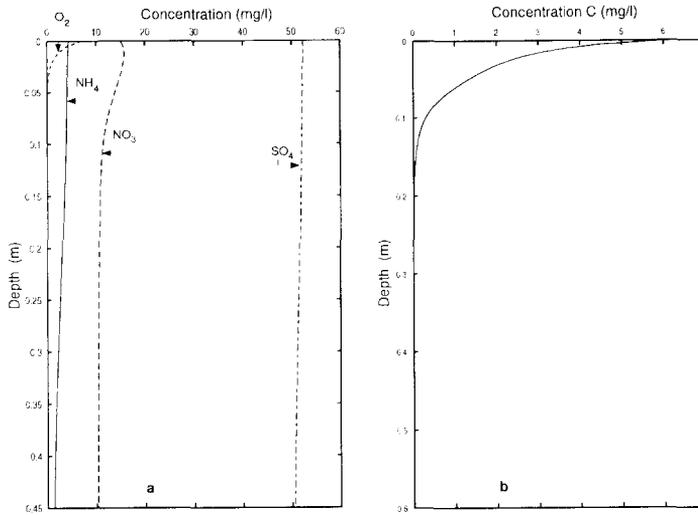
Fig. 17. Simulated test case where no solubilisation of solid organic matter occurs in the sediment: (a) oxygen, nitrate, sulfate and ammonium concentration profiles; and (b) dissolved organic carbon concentration profile in sediments.

These figures are in line with the scant data from experimental bank-filtration sites found in the literature. For example, at the well-known experimental infiltration site on the river Glatt in Switzerland (Hoehn et al., 1983; Schwarzenbach et al., 1983; Jacobs et al., 1988), solid organic matter in the sediment amounts to < 0.5%, whereas the water flux velocity is ~ 2 m/day. As might be expected, nitrate concentration in the aquifer, near the bank is 5–10 mg/l compared to ~ 30 mg/l in the Glatt river and ammonium is found at low concentration in the aquifer (≤ 0.3 mg/l). In another study of a bank-filtration site in France (near the Rhône river), described by Ille (1992), the organic carbon in the river sediments is ~ 1% whereas the flux of percolating water is in the range of 4–6 m/day. Similarly, the nitrate concentration is low (0–1 mg/l in the aquifer near the bank compared to 5–10 mg/l in the river) as is the ammonium concentration (~ 0.3 mg/l). In contrast, at the site we investigated, the amount of organic carbon in the river sediment is between 1% and 7% and the velocity of percolating water varies between a few mm/day and 15 cm/day. No nitrate was found in the aquifer and ammonium shows high concentrations near the bank (from 6 to 20 mg/l).

6. Summary and conclusions

In many countries, water pumped in alluvial aquifers hydraulically connected to a river is an important source of drinking water both from a quantitative and qualitative point of view. It is therefore essential to know what chemical changes may occur in the water during its transfer from the river to the aquifer. We have presented some data on

the effect of bank-filtration at an experimental site located along a heavily polluted river. The major feature of this site is the great difference in chemical composition of the water in the river and in the aquifer. It appears that here bank-filtration induces very strong reducing conditions. Among others, nitrate disappeared from the aquifer whereas ammonium and iron were observed in the bank-filtrated water in much higher concentrations than in the river water. This evolution of bank-filtrated water towards more reducing conditions is the result of intense bacterial activity involving organic carbon mineralization. The river bed sediments, acting as an interface between river water and groundwater, are preferred sites for this microbial activity. A conceptual and numerical model was developed to simulate the important biogeochemical changes during bank-filtration with an emphasis on nitrogen compounds. We assume that many of the changes undergone by bank-filtrated water occur in the first few meters of infiltration into the river bed. The evolution of the water chemistry during the transfer through the sediments is represented by consumption/production of mineral electron acceptors (oxygen, nitrate, sulfate) coupled with organic matter degradation. Bacteria play an essential role in these processes as they consume organic matter to produce energy and growth. This benthic bacterial activity is explicitly taken into account in the model. The coupled system of transport equation and biochemical reactions is solved numerically by a time-splitting procedure. The model can reproduce the results by von Gunten and Zobrist (1993) obtained with column experiments designed to simulate infiltration into an aquifer of an organically polluted river containing multiple electron acceptors. The results of the model are in agreement with the observed data. Two parameters appear to be of primary importance for the evolution of the filtrate chemistry, in particular where nitrogen species are concerned: the percolation velocity of the water through the river sediments and organic matter content in these sediments. An increase in water velocity allows the electron acceptors to penetrate more deeply into the sediment, diminishes the extent of the anaerobic mineralization zone and attenuates the reducing conditions in the aquifer. The influence of sedimentary organic carbon on the mineralizing capacities of the benthic microfauna depends on the amount initially present in the sediment and the exoenzymatic solubilisation possibilities. In the case studied here, low water velocity combined with high inputs of particulate organic carbon from sewage treatment plants lead to severe reducing conditions in the aquifer with ammonium accumulation in the river bed sediments.

7. Notation

b	decay rate constant of bacteria	$[T^{-1}]$
C_{sat}	carbon saturation concentration in pore water	$[M\,L^{-3}]$
D	hydrodynamic dispersion coefficient	$[L^2\,T^{-1}]$
D_s	mixing coefficient of solid phase	$[L^2\,T^{-1}]$
DOC^1, DOC^2	Two types of dissolved organic carbon	$[M\,L^{-3}]$
K_{CO}^i, K_{CN}^i, K_{CS}^i, K_{Ni}	half-saturation constants for organic carbon	$[M\,L^{-3}]$

K_O, K_N, K_S half-saturation constants for O_2, NO_3 and SO_4, $[M \, L^{-3}]$
respectively
K_{ON}^i, K_{NS}^i, K_{OS}^i,   inhibition constants for NO_3, SO_4 and CH_4, $[M \, L^{-3}]$
K_{SC}^i respectively
k_{sol} solubilisation coefficient for solid organic carbon $[L^3 \, M^{-1} \, T^{-1}]$
L advection–dispersion differential operator
SOC   solid organic carbon $[M \, L^{-3}]$
U Darcy velocity $[L \, T^{-1}]$
Y_O, Y_N, Y_S, Y_{CH_4} yield coefficients for O_2, NO_3, SO_4 and CH_4,
respectively
β_O, β_N, β_S, β_C stoichiometric coefficient for carbon utilization
γ exchange coefficient between mobile and $[T^{-1}]$
immobile phase
λ_{Ni}, λ_{NO_3},   stoichiometric coefficient for ammonium and
nitrate production, respectively
ω_m mobile phase porosity
μ_O^i, μ_N^i, μ_S^i, μ_C^i maximum specific growth rate for O_2, NO_3, SO_4 $[T^{-1}]$,
and CH_4 respirations, respectively
ρ bacteria concentration $[M \, L^{-3}]$

Acknowledgements

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