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1 **Nutrient cycling in bedform induced**
2 **hyporheic zones.**

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Abstract

The hyporheic zone is an ecotone connecting the stream and groundwater ecosystem that plays a significant role for stream biogeochemistry. Water exchange across the stream-sediment interface and biochemical reactions in the streambed concur to affect subsurface solute concentrations and eventually nutrient cycling in the fluvial corridor. In this paper we investigate the interplay of hydrological and biochemical processes in a duned streambed and their effect on spatial distribution of solutes. We employ a numerical model to simulate the turbulent water flow and the pressure distribution over the dunes, and then to evaluate the flow field and the biochemical reactions in the hyporheic sediments. Sensitivity analyses are performed to analyze the influence of hydrological and chemical properties of the system on solute reaction rates. The results demonstrate the effect of stream velocity and sediment permeability on the chemical zonation. **Changing sediment permeability as well as stream velocity directly affects the nutrient supply and the residence times in the streambed, thus controlling the reaction rates under the dune.** Stream water quality is also shown to influence the reactive behavior of the sediments. In particular, the availability of dissolved organic carbon determines whether the streambed acts as a net sink or source of nitrate. This study represents **a step towards** a better understanding of the complex interactions between hydrodynamical and biochemical processes in the hyporheic zone.

1 INTRODUCTION

Majority of the world's rivers transports high levels of nutrients, such as organic carbon, nitrate and phosphate, due to anthropogenic activities (Boyer et al., 2006; Mulholland et al., 2008). In the last decades, the fate of these nutrients has attracted the interest of several researchers and, in particular, many studies have shown the significant role played on nutrient cycling by the exchange processes with the hyporheic zone, i.e. the interface region between stream water and groundwater (e.g., Findlay, 1995; Brunke et al., 1997; Boulton et al., 1998; Tonina and Buffington, 2009a).

The hyporheic fluxes occur generally in response to variations in bed topography (Tonina and Buffington, 2009b), with a very wide range of spatial and temporal scales (Cardenas, 2008b; Stonedahl, 2010). Small-scale exchanges are mainly induced by river bed forms, like ripples and dunes (Elliott and Brooks, 1997a,b; Packman et al., 2001; Packman et al., 2004; Boano et al., 2007; Cardenas and Wilson, 2007), while large-scale exchanges depend on larger geomorphological features, like pool-riffle pairs (Tonina and Buffington, 2007), step-pool sequences (Harvey and Bencala, 1993) or meander bends (Boano et al., 2006; Cardenas, 2008a,b; Revelli et al., 2008).

The exchange of water and solutes across the streambed has an effect on the ecology of the fluvial environment since it contributes to the connection of surface and subsurface waters, which have very different chemical characteristics. The exchanged chemicals enter the sediments with the water and they are transformed into oxidized or reduced substances by biogeochemical reactions, mediated by the hyporheic **microbiota**. In particular, organic substances are used as electron donors in a series of redox reactions, with different electron acceptors, e.g., oxygen and nitrate. Nitrification and other secondary reactions often occur as soon as water enters the hyporheic zone (Hunter et al., 1998). These sediment-scale transformations have an influence on the quality of the upwelling water and potentially also on the quality of the stream water. **For example, Böhlke et al. (2009) demonstrated with field measurements that benthic denitrification contributes substantially to nitrate removal in streams.**

The interaction of hydrology and biogeochemistry in the hyporheic zone was taken into

60 account in different studies of both fluvial (e.g., Gu et al., 2007; Lautz and Fanelli,
61 2008; O'Connor and Hondzo, 2008) and marine (e.g. Meysman et al., 2007)
62 environments. In particular, Harvey and Fuller (1998) and Fuller and Harvey
63 (2000) provided observations of solute concentration gradients and reaction
64 rates beneath bedforms in real streams, determining the role of the hyporheic
65 zone in enhancing microbially mediated processes. Recently, mathematical models
66 have been increasingly used to investigate the effect of coupled hydrological and biogeo-
67 chemical processes on the fate of nutrients. For instance, Cardenas et al. (2008) provided
68 a model for a rippled permeable seabed, by sequentially modeling turbulent-oscillatory
69 flow, porous media flow, and biogeochemical reactions. Another modeling approach was
70 suggested by Boano et al. (2010), who investigated the biogeochemical patterns and the
71 temporal evolution of reactive solutes in the hyporheic region of a meandering river, by
72 estimating and comparing the typical kinematic and chemical timescales. However, we
73 are still far from a complete understanding of the complex links between hydrodynamical
74 and biogeochemical processes in the hyporheic zone (Fleckenstein et al., 2010).

75 In this paper, we focus on the influence of surface water-groundwater exchange on the
76 main microbial transformations of nutrients occurring in the hyporheic zone. In particular
77 we develop a numerical model to analyze the exchange triggered by a duned streambed,
78 that represents a widespread configuration in fluvial environments. Our aim is to shed
79 light on the effects of this kind of bed forms on transport and reaction processes of organic
80 carbon and nitrogen, in order to provide significant insights for stream biogeochemistry.
81 The main results of the study are the description of the steady-state spatial distribution
82 of water-borne solutes below a stream dune and the analysis of the effects of stream water
83 quality, stream velocity, and sediment permeability on the reaction patterns. In particular,
84 we take into account four representative reactive compounds: dissolved organic carbon
85 (DOC), oxygen (O_2), nitrate (NO_3^-) and ammonium (NH_4^+). We chose these chemicals
86 because they are usually used as indicators of water quality in field studies (Aitkenhead-
87 Peterson et al., 2009) and they have a direct influence on the equilibrium of the river
88 ecosystem.

89 The paper is divided in two parts, i.e. the model description, followed by the sensitivity
90 analyses. The simulation of the turbulent water flow represents the preliminary step for the
91 modeling: we numerically solve the Reynolds-Averaged Navier Stokes (RANS) equations
92 in order to obtain the pressure distribution over the dunes. Then, given the RANS-
93 derived surficial pressure gradients, the hyporheic flow field is obtained by applying the
94 Darcy's law. Longitudinal groundwater flow, induced by the stream bed slope, is also
95 considered. The biogeochemical two-dimensional model is finally applied by coupling the
96 chemical reactions with both the hyporheic advective flow field and fluxes induced by
97 hydrodynamic dispersion, under appropriate boundary conditions.

98 The sensitivity analyses of the biochemical model are carried out for different hydrody-
99 namic and chemical configurations. We study the effect of stream velocity, surface water
100 chemistry, and sediment characteristics on the nutrient dynamics, in order to better un-
101 derstand the links between the hydrodynamic processes and the nutrient transformation
102 rates in the hyporheic zone.

103

104 2 MODEL DESCRIPTION

105 The problem of interest is sketched in Fig. 1. We consider a stream with mean water
106 depth, d , and bulk velocity, U . The streambed is formed of two-dimensional periodic dunes,
107 triangular in shape, with height H and length L . The dunes are asymmetric because of the
108 constant direction of the stream flow, and the position of the crest (L_c) is shifted towards
109 the downstream end of the dune. A Cartesian reference system is adopted, with x and y
110 as the streamwise and upward coordinates, respectively, and the axis origin is placed at
111 the dune trough. Due to the periodicity of the streambed in the streamwise direction, we
112 focus on a single-dune cell of the 2D domain.

113 The goal is to estimate the spatial distribution of four solutes under the bed forms in
114 steady-state conditions, given the physical and chemical properties of the stream and the
115 hydraulic properties of the sediments. First, turbulent flow in the stream is simulated,
116 and values of pressure on the streambed are evaluated. Then, we numerically simulate

117 the solute concentrations below the dune surface by considering both the advective and
 118 dispersive flows and the biochemical processes. The compounds of interest are DOC,
 119 oxygen, nitrate and ammonium. We chose formaldehyde (CH_2O) to represent the DOC
 120 substance for its simple chemical structure and because it can be a degradation product of
 121 more complicated DOC compounds. Moreover, it is usually selected as the representative
 122 DOC compound for numerical simulations or field investigations concerned with the study
 123 of chemical patterns in water (e.g., Hunter et al., 1998).

124 The governing equations and the modeling scheme of the pressure distribution, the
 125 hyporheic flow field and the biogeochemical reactions are described below.

126 2.1 Pressure Distribution

127 The turbulent water flow over the dunes is simulated by numerically solving, in steady-
 128 state conditions, a finite-volume formulation of the Reynolds-averaged Navier-Stokes (RANS)
 129 equations for an incompressible, homogeneous fluid (Cardenas and Wilson, 2007)

$$\frac{\partial U_i}{\partial x_i} = 0 \quad (1)$$

130

$$\rho U_j \frac{\partial U_i}{\partial x_j} = -\frac{\partial P}{\partial x_i} + \frac{\partial}{\partial x_j} \left(2\mu S_{ij} - \rho \overline{u'_j u'_i} \right) \quad (2)$$

131 where $i, j = 1, 2$ are spatial indexes corresponding to x and y directions ($x_1 = x, x_2 = y$),
 132 ρ and μ are water density and dynamic viscosity, respectively, t is time, U_i and u'_i are the
 133 time-averaged and turbulent velocity components in x_i direction, respectively, and P is
 134 time-averaged pressure. $S_{i,j}$ is the strain rate tensor

$$S_{i,j} = \frac{1}{2} \left(\frac{\partial U_i}{\partial x_j} + \frac{\partial U_j}{\partial x_i} \right), \quad (3)$$

135 while $-\overline{u'_j u'_i} = \tau_{ij}/\rho$ is the mean strain rate related to the Reynolds stresses (τ_{ij}) by

$$-\overline{u'_j u'_i} = \nu_t (2S_{ij}) - \frac{2}{3} \delta_{ijk} \quad (4)$$

136 where ν_t is the kinematic eddy viscosity, δ_{ij} is the Kronecker delta, and k is the turbulent
 137 kinetic energy.

138 The evaluation of the turbulent strain rates requires the adoption of a closure scheme
 139 to determine the eddy viscosity ν_t . Here, the $k - \omega$ turbulence closure scheme (Wilcox,
 140 1991) is adopted, with the eddy viscosity

$$\nu_t = \frac{k}{\omega}, \quad (5)$$

141 the specific dissipation ω ,

$$\omega = \frac{\epsilon}{\beta^* k} \quad (6)$$

142 the turbulence dissipation rate ϵ , and the closure coefficient β^* .

143 Two additional equations for k and ω are required to complete the closure scheme. The
 144 steady state transport equations for k and ω are

$$\rho \frac{\partial (U_j k)}{\partial x_j} = \rho \tau_{ij} \frac{\partial U_i}{\partial x_j} - \beta^* \rho \omega k + \frac{\partial}{\partial x_j} \left[(\mu + \mu_t \sigma_k) \frac{\partial k}{\partial x_j} \right] \quad (7)$$

145

$$\rho \frac{\partial (U_j \omega)}{\partial x_j} = \alpha \frac{\rho \omega}{k} \tau_{ij} \frac{\partial U_i}{\partial x_j} - \beta \rho \omega^2 k + \frac{\partial}{\partial x_j} \left[(\mu + \mu_t \sigma_\omega) \frac{\partial \omega}{\partial x_j} \right] \quad (8)$$

146 The standard closure coefficient values are $\alpha = 5/9$, $\beta = 3/40$, $\beta^* = 9/100$, and $\sigma_k = \sigma_\omega$
 147 $= 0.5$ (Cardenas and Wilson, 2007).

148 The RANS domain is represented by the water column above a single dune (Fig. 1).
 149 **A spatially periodic pressure condition is prescribed on the lateral boundaries,**
 150 **with an additional pressure drop ΔP between the left and right domain sides,**
 151 **in order to consider the stream gradient. We assume therefore that the water**
 152 **columns over two subsequent dunes exhibit the same pressure distribution**
 153 **and a constant difference in magnitude, with lower values downstream. The**
 154 **pressure drop is derived from the bed slope i_b and the dune length L by**
 155 **applying the equation $\Delta P = i_b L g \rho$. A symmetry boundary condition (i.e., no**
 156 **fluxes) is set at the top of the RANS domain since water depth is significantly**
 157 **larger than the dune height ($d \ll H$) and the submergence is high. Thus, the**

158 free surface is not influenced by the presence of bed forms and it is possible
159 to replace it with the symmetry condition. Finally, no-slip wall boundary
160 conditions ($U_j = 0$) are applied at the bottom of the domain. This allows us to
161 solve the problem for turbulent flow neglecting the influence of the subsurface
162 flow in the sediments on the surface flow, which is a standard assumption since
163 subsurface flow rates are usually much smaller than those in the stream. The RANS
164 simulations are solved using a finite-volume approach with a variable number of grid
165 elements (from 16000 to more than 80000) and a denser node spatial distribution near the
166 bottom of the domain. For further details see Cardenas and Wilson (2007).

167 From the solution of the RANS model, the pressure distribution on the duned streambed
168 is obtained. Fig. 2 shows some streambed pressure distributions on a 1-meter-long dune
169 for different values of the Reynolds number $Re = U \cdot d/\nu$, where ν is the kinematic wa-
170 ter viscosity. All pressure profiles have an asymmetrical shape, with a maximum at $x =$
171 0.3 m and a marked minimum at the dune cres ($x = 0.9$ m). The figure shows that an
172 increase of the stream velocity leads to higher values of surface pressures. The resulting
173 pressure gradients determine the water exchange with the sediments, as described in the
174 next section.

175 2.2 Hyporheic Flow Field and Biochemical Reactions

176 The pressure distribution over the dune is used as a boundary condition in the multi-
177 component reactive transport model in order to predict the solute fluxes and concentra-
178 tions in the hyporheic zone, considering both the fluid dynamics and chemical processes.
179 For this purpose, the hyporheic flow modeling represents a key step, since it determines
180 the advective and dispersive transport patterns of the substances in the hyporheic zone.

181 The advective exchange of water across a duned streambed can be driven by two
182 mechanisms of “pumping” and “turnover”: the former is due to the presence of pressure
183 gradients over the bed forms, the latter is linked to the temporary trapping and release
184 of water by moving bed forms (Elliott and Brooks, 1997a). In this paper we assume that
185 the dunes are not moving, since preliminary numerical simulations (not shown) indicated

186 that water fluxes induced by turnover are negligible for our system.

187 The water flow under the bed surface in steady-state conditions is estimated using the
188 groundwater flow equations, i.e., the Darcy's law and the continuity equation

$$\mathbf{q} = -\frac{\kappa}{\mu} (\nabla P + \rho g \nabla y) \quad (9)$$

189

$$\nabla^2 \left(\frac{P}{\rho g} + y \right) = 0, \quad (10)$$

190 where $\mathbf{q} = (q_x, q_y)$ is the Darcian velocity vector, κ is the permeability of the porous
191 medium (assumed homogeneous), g is the gravitational acceleration, ρ is the water density,
192 and P is the water pressure in the porous medium. **The velocity \mathbf{q} includes both the**
193 **pumping-induced flow and the basic groundwater flow, the latter due to the**
194 **stream gradient.** The pressure boundary conditions are described later.

195 As to the biochemical processes, the model considers three reactions, mediated by sub-
196 surface microorganisms: **aerobic respiration, denitrification and nitrification** (see
197 **Table 1).** **Reactions r_1 and r_2 describe the heterotrophic DOC biodegradation,**
198 **with the DOC as the electron donor and the oxygen (aerobic respiration)**
199 **and nitrate (denitrification) as the electron acceptors, respectively. Reaction**
200 **r_3 represents nitrification, i.e., the biological autotrophic oxidation of ammo-**
201 **nium into nitrate, with oxygen as electron acceptor. Aerobic respiration and**
202 **nitrification start simultaneously, while denitrification only occurs when oxy-**
203 **gen concentration falls under a limiting value, i.e. when anaerobic conditions**
204 **are established.**

205 For the definition of the reaction kinetics we follow the approach described by Hunter
206 et al. (1998) and, for redox reactions r_1 and r_2 , we consider separately the rate of DOC
207 oxidation and the rate of the i -th reduction half-reaction.

208 First-order degradation kinetics is assumed for the DOC oxidation rate Γ_{DOC}

$$\Gamma_{DOC} = k_{DOC} \cdot C_{DOC} \quad (11)$$

209 where k_{DOC} is the DOC decay constant and C_{DOC} is the DOC molar concentration. The
 210 linear kinetics in equation (11) is the simplest way to model DOC degradation, but it
 211 could be replaced by more complex formulations (e.g., Monod) at the expense of a higher
 212 number of parameters.

213 The rate of reduction $\Gamma_{red,i}$ of the i -th electron acceptor ($i = 1$ for oxygen, $i = 2$ for
 214 nitrate) is estimated by

$$\Gamma_{red,i} = \beta_i \cdot \Gamma_{DOC} \cdot f_i \quad i = 1, 2 \quad (12)$$

215 where β_i represents the ratio between the moles of transferred electrons per mole of
 216 oxidized DOC and the moles of electrons per mole of reduced compound in the i -th
 217 reaction, and f_i is the fraction of electrons consumed by the i -th reduction half-reaction.
 218 Values of β_i are given in Table 1. The f_i parameter is evaluated with a simplified Monod
 219 formulation

$$f_i = \left(1 - \sum_{n=0}^{i-1} f_n \right) \cdot \alpha_i \quad (13)$$

220 **with $f_0 = 0$ and**

$$\alpha_i = \begin{cases} \frac{C_i}{C_{i,lim}} & \text{if } C_i < C_{i,lim} \\ 1 & \text{if } C_i \geq C_{i,lim} \end{cases} . \quad (14)$$

221 α_i is a dimensionless parameter that considers the limitation of $\Gamma_{red,i}$ due to the availability
 222 of the i -th reaction electron acceptor, while C_i and $C_{i,lim}$ are, respectively, the molar
 223 concentration and the molar limiting concentration of the i -th reaction electron acceptor.

224 **When the electron acceptor exceeds the limiting concentration, the reduction**
 225 **rate is independent of C_i , while in the case of lower concentrations $\Gamma_{red,i}$ is**
 226 **linearly proportional to C_i .**

227 Lastly, a bimolecular expression is used for the nitrification (r_3) rate Γ_{nitr}

$$\Gamma_{nitr} = k_n \cdot C_{NH_4^+} \cdot C_{O_2} \quad (15)$$

228 where k_n is the second-order nitrification molar rate coefficient, $C_{NH_4^+}$ and C_{O_2} are the

229 molar concentrations of ammonium and oxygen, respectively. **Since the aim of the**
 230 **present work is to study the reactive behavior of hyporheic sediments in re-**
 231 **sponse to stream water quality and velocity and to sediment properties, we**
 232 **neglect the influence of temperature on reaction kinetics.**

233 From equations (11–14) we define the net production rates of the four compounds of
 234 interest, adopting a negative sign for reaction terms decreasing the solute concentration

$$\frac{dC_{DOC}}{dt} = -\Gamma_{DOC} \equiv R_{DOC} \quad (16)$$

$$\frac{dC_{O_2}}{dt} = -\Gamma_{red,1} - 2\Gamma_{nitr} \equiv R_{O_2} \quad (17)$$

$$\frac{dC_{NO_3^-}}{dt} = -\Gamma_{red,2} + \Gamma_{nitr} \equiv R_{NO_3^-} \quad (18)$$

$$\frac{dC_{NH_4^+}}{dt} = -\Gamma_{nitr} \equiv R_{NH_4^+} \quad (19)$$

235 DOC and ammonium show a negative one-term equation (eqns. (16) and (19)), since
 236 they take part as reactants in one process, DOC oxidation half-reaction and nitrification,
 237 respectively. Instead, oxygen and nitrate display double-term expressions (eqns. (17) and
 238 (18)), with different signs because they act, with different roles, in two reactions. The
 239 oxygen is consumed by both aerobic respiration r_1 and nitrification r_3 , while nitrate is
 240 removed by denitrification r_2 and **produced** by nitrification r_3 . The contribution of the
 241 different terms varies in time, according to the reactant concentrations.

242 The overall reaction rates (eqns. (16–19)) are then coupled with the hyporheic flow
 243 field (obtained by equations (9) and (10)) and hydrodynamic dispersion in order to define
 244 the governing equations of the steady-state reactive solute transport model

$$\theta R_s = \nabla(-\theta \mathbf{D} \nabla C_s + \mathbf{q} \cdot C_s) \quad s = \text{DOC}, O_2, NO_3^-, NH_4^+ \quad (20)$$

245 where θ is the sediment porosity, R_s is the consumption/**production** rate of the com-

246 pound s , \mathbf{D} is the hydrodynamic dispersion tensor and C_s is the molar concentration of
 247 the chemical s . The expressions (20) are valid in steady-state conditions and under the
 248 assumptions of no sorption phenomena and no solute source in the porous medium. Disper-
 249 sion represents a solute transport process, additional to the advective one, contributing
 250 to the spreading of the chemicals in the hyporheic zone. In particular, hydrodynamic
 251 dispersion combines mechanical dispersion, induced by the local velocity variations, and
 252 molecular diffusion, caused by concentration gradients at microscopic level. The elements
 253 of the dispersion tensor are (Bear and Verruijt, 1998)

$$\theta D_{ij} = (\alpha_L - \alpha_T) \cdot \frac{q_i q_j}{|\mathbf{q}|} + \delta_{ij} \cdot (\alpha_T |\mathbf{q}| + \theta \cdot \tau D_{mol}) \quad (21)$$

254 where $i, j = 1, 2$, α_L and α_T are the longitudinal and transversal dispersivities, respectively,
 255 τ is the tortuosity factor, and D_{mol} is the molecular diffusion coefficient. The values of
 256 the dispersivities α_L and α_T depend on sediment size and heterogeneity of the porous
 257 medium.

258 The biogeochemical model domain is a single dune, triangular in shape (see Fig. 2). As
 259 to the boundary conditions, we impose on the lateral boundaries the periodic conditions

$$P(x_{min}, y) = P(x_{max}, y) + \Delta P \quad (22)$$

260

$$C_s(x_{min}, y) = C_s(x_{max}, y) \quad (23)$$

261 with x_{min} and x_{max} as the horizontal coordinates of the initial and terminal points of the
 262 dune and ΔP as the pressure drop between the lateral boundaries of the domain, **equal**
 263 **to that one applied to the free surface.**

264 On the upper layer, i.e., on the sediment-water interface, we prescribe a Dirichlet con-
 265 dition with the RANS-derived pressure distribution and the constant solute concentrations
 266 in the stream. Finally, a no flow condition is applied to all the chemicals at the bottom
 267 of the dune, and the porous media is chosen deep enough so as not to affect the pathlines
 268 in the main zone of study, close to the bed surface.

3 RESULTS

270 The chemical zonation in the streambed is investigated through the numerical simula-
 271 tion of the governing equations of the reactive solute transport model. For this purpose,
 272 we employ a numerical code that uses a finite-volume approach, with adaptive meshing
 273 and error control. In particular, we choose a non uniform mesh, with a higher node density
 274 in the zone of interest, near the bed surface, for a total number of 3781 grid nodes and
 275 7216 triangular elements.

276 We consider a typical dune triangular geometry, with a length $L = 1$ m, a bed form
 277 height $H = 0.075$ m and the crest located at $L_c = 0.9$ m (asymmetric dune, see Fig. 1).
 278 The streambed is homogeneous and isotropic, with a porosity $\theta = 0.4$ and a tortuosity
 279 factor $\tau = 0.74$, while the mean water depth, d , is 0.5 m. With regard to the reaction
 280 constants, we choose values within the ranges suggested by Van Cappellen and Wang
 281 (1996). In order to consider a typical average condition, for the nitrification rate con-
 282 stant we use the value $k_n = 5 \cdot 10^{-6}$ L/(mg s), while for the DOC reaction rate we select
 283 $k_{DOC} = 5 \cdot 10^{-6}$ s⁻¹. Oxygen and nitrate limiting concentrations ($C_{O_2,lim}$ and $C_{NO_3^-,lim}$)
 284 are set at 1 mg/L and 0.5 mg/L, respectively. As to the other physical and chemical
 285 parameters, i.e., the in-stream solute concentrations, the stream velocity U , the sediment
 286 permeability κ and dispersivities α_L and α_T , we perform a sensitivity analysis in order to
 287 investigate their impact on the biochemical processes in the streambed.

288

289 3.1 Impact of Stream Water Quality

290 Three configurations, characterized by different values of in-stream solute concentrations
 291 (see Table 2), are considered: a polluted stream, with high nutrient concentrations (case
 292 1), a pristine stream with no DOC limitation (case 2) and a pristine stream with DOC
 293 limitation (case 3). **The pristine stream configuration is split in two cases in**
 294 **order to consider the remarkable effects of DOC availability on the kinetics**
 295 **of reactions.** The permeability κ is set equal to 10^{-10} m², characteristic of well-sorted
 296 coarse sands to gravels. The longitudinal dispersivity is assumed equal to 3 mm (i.e., a
 297 few grain diameters), while the transversal dispersivity α_T is a tenth of the longitudinal

298 one α_L . The stream velocity U is 0.34 m/s and the stream slope is $1.5 \cdot 10^{-4}$.

299 The results of the simulations are displayed in Fig. 3 (case 1), 4 (case 2) and 5 (case 3).
300 Two advective flow cells are visible below the streambed surface, with different width and
301 depth. The cell in the right-hand part of the dune is wide and quite deep (65 cm); mean
302 flow direction in the cell is the same as the stream flow. On the contrary, the left cell is
303 narrower and shallower, with mean flow opposite to the stream flow. A stagnation point
304 is also present at the deepest point of this cell. Both advective cells delimit an advective
305 water exchange area, where water from the stream moves along advective flowpaths before
306 leaving the sediments, with different residence times depending on path length. Beneath
307 this zone the flow field is dominated by groundwater underflow, induced by the stream
308 slope, and water flow is not affected by the presence of the dunes. **The same reversed**
309 **hyporheic circulation cells and flow stagnation zones were recently observed**
310 **in a flume and modeled by CFD from Endreny et al. (2011). The flow cells**
311 **have a direct influence on solute spatial distribution. In fact, even though**
312 **dispersion tends to smooth concentration gradients, the solute concentration**
313 **fronts clearly reflect the shape of the water exchange area.**

314 The substantial role played by advection and dispersion fluxes is demon-
315 strated in Fig. 6, where oxygen concentrations of case 2 are shown for different
316 dune vertical sections, in the case of diffusive transport only, i.e., switching
317 off water flow and the resulting advective and dispersive fluxes. Oxygen pen-
318 etration in the porous medium occurs with such a low velocity that the com-
319 pound is completely removed within the first 5 millimeters of sediments in all
320 the considered sections. Another key point is that the diffusive transport is
321 downward directed, so all solutes entering the sediments are slowly moved to
322 deeper layers and are not returned back to the stream. Thus, the advective
323 and dispersive fluxes are fundamental for controlling the nutrient fate in the
324 streambeds.

325 We now analyze the three basic cases to investigate the effect of stream
326 water quality. We consider at first the polluted stream configuration shown in Fig. 3.

327 DOC exhibits a smooth spatial distribution, with two roughly circular fronts of different
328 sizes and concentrations decreasing with depth. In fact, both advection and dispersion
329 are important mechanisms for delivery of DOC into the porous medium, **where it is**
330 **progressively degraded (eqn. (16))**. Thus, the hyporheic zone acts as a sink of DOC
331 for the stream. However, the DOC is still present at the bottom of the dune with a
332 concentration of 30 mg/L, since it is not a limiting reactant for the two reactions.

333 Oxygen displays a similar behavior, with concentration decreasing with depth. How-
334 ever, oxygen fronts are steeper than DOC ones, because of the fast oxygen consumption by
335 two contemporary reactions, i.e., **aerobic respiration and nitrification (eqn. (17))**.
336 Moreover, due to the low in-stream oxygen concentration and the high availability of
337 DOC and NH_4^+ , oxygen is completely removed within the first 30 cm of depth, i.e. within
338 the water exchange area. **These simulated oxygen distributions reproduce well**
339 **the general features of the patterns observed experimentally by Precht et al.**
340 **(2004)**.

341 Ammonium also exhibits steep fronts and remarkable variations of concentration in the
342 hyporheic zone, because of the fast kinetics of the nitrification process in which it plays
343 the part of the reactant (eqn. (19)). Eventually, a concentration of 4.5 mg/L is achieved
344 when **nitrification** stops due to the lack of oxygen. Thus, ammonium spatial distribution
345 is strictly related to the oxygen zonation.

346 A different behavior is shown by nitrate, which exhibits a maximum concentration
347 at 15 cm of depth (see Fig. 3). The reason for this behavior is that the compound has
348 the double role of product and reactant in the nitrification and denitrification reactions,
349 respectively (eqn. (18)). The removal of nitrate through denitrification begins only when
350 the oxygen falls below the limiting concentration $C_{O_2,lim}$, so up to that threshold the
351 compound is only **produced** by nitrification. **In deeper sediments, denitrification**
352 **prevails and nitrate is completely removed within the first 35 cm of depth.**
353 **This behavior is confirmed by Fig. 7a and 7b, that show the spatial patterns**
354 **of nitrification and denitrification rates. Nitrification rate has a maximum**
355 **value (0.34 mg/(m³ · s)) near the streambed, due to the high concentrations**

356 of oxygen and ammonium, and it decreases with depth, as the consequence
357 of the lower reactant concentrations. Instead, denitrification rate displays a
358 downward increase, together with the nitrate concentrations, a maximum value
359 ($0.38 \text{ mg}/(\text{m}^3 \cdot \text{s})$) at approximately 35 cm of depth and a fast decrease. Both
360 reactions are active in the central part of the domain, with different rates; as
361 long as nitrification prevails on denitrification there is a net nitrate production
362 and viceversa. The strong nitrate production within the first 20 cm of depth
363 contributes to enhance the nitrate concentration gradient and, consequently,
364 the upward dispersive fluxes (see equation (20)), that are comparable or higher
365 than the advective ones, with the exception of the dune crest (see Fig. 7c,
366 7d, 7e, 7f). Part of produced nitrate is released into the stream due to the
367 combination of strong upward advective and dispersive transport, and the
368 dune thus represents a source of nitrate for the stream.

369 We focus now on the pristine stream configuration with no DOC limitation (case 2,
370 Fig. 4). All solute in-stream concentrations are lower than in the polluted case, with the
371 exception of oxygen, which keeps the same value (Table 2). The decrease of the solute
372 concentrations has a direct influence on the rate of the three studied reactions. Oxygen
373 shows a more gradual decay and wider concentration fronts, due to the decrease of both
374 aerobic respiration and nitrification rates caused by lower concentrations of DOC and
375 ammonium, respectively. The slower oxygen consumption leads in turn to a downward
376 shift of the net denitrifying zone. Thus, nitrate and oxygen are completely
377 removed deeper in the porous medium than in case 1. The spatial patterns of
378 nitrification and denitrification rates are shown in Fig. 8a and 8b. The values
379 are in general one or two orders of magnitude lower than those seen for case 1.
380 Besides, the maximum nitrification rate is highly lower than the denitrification
381 one. The lower nitrate production has a direct effect on the magnitude of the
382 dispersive transport of nitrate. Fig. 8c, 8d, 8e and 8f show the advective and
383 dispersive fluxes with the former prevalent on the latter in the shallow layers.
384 In this case the dune represents a sink of nitrate for the stream.

385 The wider concentration fronts are even more evident for the pristine stream configu-
 386 ration with DOC limitation (case 3, Fig. 5). **Aerobic respiration** rate is so slow, due
 387 to the DOC scarcity, that oxygen can be found even at the bottom of the streambed (6
 388 mg/L), preventing the denitrification process which requires anaerobic conditions. **Thus,**
 389 **denitrification does not occur in the sediments in this case. Aerobic respi-**
 390 **ration is active up to the bottom of the streambed, while nitrification stops**
 391 **shallower, at 60 cm of depth, for lack of ammonium. For this reason nitrate**
 392 **concentrations show an increase with depth up to 60 cm of depth, while they**
 393 **keep a constant value under that layer. As seen for case 1, the hyporheic zone**
 394 **behaves as a net nitrate source because of the strong nitrate dispersive trans-**
 395 **port (induced by nitrate production), upward directed, near the bed surface.**

396 The different behavior of the hyporheic zone in the three cases is clearly underlined by
 397 the values of the Integrated oxygen Aerobic Respiration rates (IAR) and the **Nitrification**
 398 (IN) and Denitrification (ID) rates (see Table 3)

$$IAR = \int_{A_s} \Gamma_{red,1} \cdot dA, \quad (24)$$

$$IN = \int_{A_s} \Gamma_{nitr} \cdot dA, \quad (25)$$

$$ID = \int_{A_s} \Gamma_{red,2} \cdot dA, \quad (26)$$

401 where A_s is the subsurface domain area, i.e. the volume of sediments per unit
 402 stream width.

403 Table 3 shows that aerobic respiration rate IAR increases with increasing in-stream con-
 404 centrations of DOC (e.g., compare cases 2 and 3). In fact, increasing in-stream
 405 DOC concentration concurs to increase oxygen reduction rate $\Gamma_{red,1}$ (see equa-
 406 tions (11) and (12)), and thus IAR.

407 If we focus on nitrate, the ratio between ID and IN indicates the reactive
 408 behavior of the dune as a net sink ($ID/IN > 1$) or source ($ID/IN < 1$) of
 409 nitrate. This happens because there is no net solute flux through the lateral

410 boundaries due to the periodic boundary conditions, and thus net nitrate pro-
411 duction equals net exchange flux through the streambed. In Table 3 we observe
412 that the hyporheic zone can act as a net source of nitrate in both polluted and pristine
413 streams (cases 1 and 3), despite these cases representing two seemingly opposite chemical
414 conditions. The DOC availability is a discriminating parameter for the degradation rates
415 in pristine streams; **high concentrations of labile DOC enhance both aerobic res-**
416 **piration and denitrification rates, leading to a faster removal of oxygen and a**
417 **net consumption of nitrate in hyporheic sediments.**

418 3.2 Impact of Stream Velocity

419 Increasing stream velocity values are considered for the three cases in Table 2, in order to
420 estimate and compare the solute reaction rates, reflecting the behavior of the streambed.
421 The stream velocity ranges from 0.21 m/s to 0.39 m/s, which correspond to Reynolds
422 number Re between 106670 and 195630.

423 A variation of the stream velocity induces two opposite effects on solute reactions. From
424 a hydrodynamical point of view, an increase in U implies higher inward water fluxes due to
425 the higher pressure gradients on the dune surface. This leads to larger fluxes of substances
426 from the stream to the sediments which can enhance reaction rates. Nevertheless, hyporheic
427 microbes have less time for performing biochemical reactions because of the lower residence
428 time of the compounds in the streambed, potentially leading to lower reaction rates. The
429 net effect on reaction rates depends on the interaction between these opposite factors, i.e.,
430 higher solute inputs and lower residence times (Arnon et al., 2007; Cardenas et al., 2008).

431 Looking at the results (Table 4), it can be observed that all integrated solute reac-
432 tion rates increase with the stream velocity, even if with different relative variations. In
433 particular, the IN parameter shows a higher sensitivity to the stream velocity variations
434 than the other ones, with consequences on the general streambed reactive behavior. These
435 trends demonstrate **that in the simulated conditions the increase of inward solute**
436 **fluxes, with U , have a predominant role for the solute reaction rate, while the**
437 **decrease of the residence times in the porous medium is less important.**

438 As to the net nitrate production rate, we consider the ratio of ID to IN. Fig. 9
439 shows that the increase of the stream velocity does not change dramatically the streambed
440 behavior but it clearly leads to limiting the sink role (case 2), and to enhance the source
441 role (case 1) of the hyporheic zone. This behavior is the result of **a higher sensitivity**
442 **of nitrification to stream velocity, compared to denitrification.**

443 3.3 Impact of Sediment Hydraulic and Transport Properties

444 We focus on the pristine stream configuration with no DOC limitation (case 2). **Although**
445 **recently it has been demonstrated that sediment permeability heterogeneity**
446 **influences hyporheic exchange (Sawyer and Cardenas, 2009), in this section**
447 **the role of permeability is investigated, under the hypothesis of homogeneity,**
448 **for the sake of simplicity.** The stream velocity U is set to the constant value of 0.27
449 m/s, while the sediment permeabilities and dispersivities are varied to investigate the
450 influence of the size of sediment grains (see Table 5). Since dispersivity is proportional
451 to the sediment grain size, d_g , and permeability scales with d_g^2 , it follows that a ten-fold
452 increase in κ results in approximately a three-fold increase in α_L . Again, values of the
453 transversal dispersivities α_T are chosen as a tenth of the longitudinal ones.

454 The results underline a marked effect of the permeability on the solute spatial distri-
455 bution (see Fig. 10), with less steep fronts corresponding to higher values of permeability
456 and dispersivity. The increase of κ , α_L and α_T results in more efficient advective and
457 dispersive transport and enhanced solute penetration. For $\kappa = 10^{-11}$ m² DOC degra-
458 dation is fast and the compound is completely removed within the first 30 cm of depth
459 (Fig. 10a), while for $\kappa = 5 \cdot 10^{-10}$ m² high DOC values (38 mg/L) are still present at
460 the bottom of the streambed (Fig. 10d). It is also interesting to observe the different
461 streambed aerobic conditions in the opposite cases, with the aerobic zone confined in the
462 shallower layers for the low permeability case and filling almost all the porous medium for
463 the high permeability case.

464 The integrated reaction rates show an increase with increasing sediment permeability
465 (Table 5), with different sensitivities. This behavior is caused by the higher nutrient supply

466 from the stream with increasing permeability, and is similar to the effect of increasing
467 stream velocity. Values of IN show that nitrification, more than denitrification, is sensitive
468 to permeability, which leads to a shift from the hyporheic zone acting as a net nitrate sink
469 ($ID/IN > 1$) to source ($ID/IN < 1$) with increasing κ .

470 4 CONCLUSIONS

471 The solute spatial distribution in the hyporheic zone is due to a strong interplay of
472 both hydraulic and biogeochemical processes. Nutrients enter the sediments because of
473 pressure-induced water exchanges, and there they are both transported by advective and
474 dispersive fluxes, and then biochemically transformed by hyporheic **microbiota**. So, a
475 variation of the transport conditions or the chemical kinetics, induced by different stream
476 and sediment characteristics, can have a direct influence on the reaction potential of the
477 streambed, **with ecological implications. If we focus on the hyporheic fauna, the**
478 **exchanges of water, nutrients and organic matter through the streambed and**
479 **the chemical concentrations in the sediments are fundamental for microbiota**
480 **and invertebrates.**

481 Our simulations show that the stream water quality can strongly affect the biochemical
482 reactions. In general, the streambed always acts as a sink of DOC, oxygen and ammonium,
483 while nitrate, that is subject to production and consumption reactions, displays a more
484 complex behavior. In the considered cases, high in-stream concentrations of solutes have
485 been shown to enhance **nitrification** process leading to strong nitrate production in the
486 porous medium. In these conditions the hyporheic zone behaves as a nitrate source for
487 the stream. In pristine streams nitrate fate has proved to be strictly linked to DOC
488 availability. A scarcity of DOC can limit denitrification and prevent nitrate removal,
489 leading to a streambed acting as a nitrate source. Instead, high concentrations of DOC
490 favour denitrification and lead to a net nitrate consumption.

491 Stream velocity and sediment permeability have displayed a direct effect on transport
492 phenomena. Increasing stream velocity implies larger solute fluxes to sediments but also
493 lower residence times of the compounds in the hyporheic zone and a lower time for reac-

494 tions. In our simulations, the higher solute supply clearly prevails over the lower residence
495 times, since all reaction rates increase with stream velocity. In particular, nitrification
496 appears to be more sensitive to changes in stream velocity than denitrification. The con-
497 sequence is that high stream velocities damp the sink role and enhance the source role
498 of the streambed. The hydraulic properties of sediments have a similar influence on so-
499 lute spatial distribution. Higher values of permeability improve the transport efficiency
500 and increase reaction rates, strongly affecting the reactive behavior of the hyporheic zone.
501 In particular, high-permeability sediments enhance nitrate production and can induce a
502 switch from nitrate sink to source behavior.

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629 197-243.

Table 1: List of the reactions considered in the simulations.

Reaction index	Reaction type	Reaction	β value
r_1	Aerobic respiration	$\text{CH}_2\text{O} + \text{O}_2 \longrightarrow \text{CO}_2 + \text{H}_2\text{O}$	1
r_2	Denitrification	$5\text{CH}_2\text{O} + 4\text{NO}_3^- + 4\text{H}^+ \longrightarrow 5\text{CO}_2 + 2\text{N}_2 + 7\text{H}_2\text{O}$	0.8
r_3	Nitrification	$\text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + 2\text{H}^+ + \text{H}_2\text{O}$	-

Table 2: Solute in-stream concentrations for cases 1, 2 and 3.

Case	$C_{\text{DOC},0}$ mg/L	$C_{\text{O}_2,0}$ mg/L	$C_{\text{NO}_3^-,0}$ mg/L	$C_{\text{NH}_4^+,0}$ mg/L
1	150	10	8	5.00
2	50.0	10	1	0.05
3	5.00	10	1	0.05

Table 3: IAR, ID and IN rates for cases 1, 2 and 3.

Case	IAR $\mu\text{g}/(\text{m}\cdot\text{s})$	ID $\mu\text{g}/(\text{m}\cdot\text{s})$	IN $\mu\text{g}/(\text{m}\cdot\text{s})$	ID/IN
-	-	-	-	-
1	106	31.4	55.9	0.56
2	49.5	1.14	0.87	1.31
3	6.14	0	1.08	0

Table 4: IAR, ID and IN rates for cases 1, 2 and 3, with different stream velocities.

Case	U	IAR	ID	IN	ID/IN
-	m/s	$\mu\text{g}/(\text{m}\cdot\text{s})$	$\mu\text{g}/(\text{m}\cdot\text{s})$	$\mu\text{g}/(\text{m}\cdot\text{s})$	-
1	0.21	78.1	26.6	38.1	0.7
1	0.24	85.8	28.1	42.8	0.66
1	0.27	93.2	29.4	47.5	0.62
1	0.30	100	30.5	52.0	0.59
1	0.33	106	31.4	55.9	0.56
1	0.36	111	32.2	59.4	0.54
1	0.39	116	32.9	62.8	0.52
2	0.21	38.3	1.05	0.62	1.68
2	0.24	41.4	1.08	0.69	1.57
2	0.27	44.4	1.11	0.76	1.47
2	0.30	47.2	1.13	0.82	1.39
2	0.33	49.5	1.14	0.87	1.31
2	0.36	51.5	1.15	0.92	1.25
2	0.39	53.4	1.15	0.96	1.19
3	0.21	4.99	0	0.80	0
3	0.24	5.32	0	0.88	0
3	0.27	5.63	0	0.95	0
3	0.30	5.91	0	1.02	0
3	0.33	6.14	0	1.08	0
3	0.36	6.33	0	1.13	0
3	0.39	6.50	0	1.18	0

Table 5: IAR, ID and IN rates for case 2, with different permeabilities and dispersivities.

$10^{11} \cdot \kappa$	α_L	α_T	IAR	ID	IN	ID/IN
m^2	mm	mm	$\mu\text{g}/(\text{m}\cdot\text{s})$	$\mu\text{g}/(\text{m}\cdot\text{s})$	$\mu\text{g}/(\text{m}\cdot\text{s})$	-
1.00	1.00	0.10	13.2	0.54	0.18	3.09
5.00	2.20	0.22	33.1	0.97	0.52	1.88
10.0	3.00	0.30	44.4	1.11	0.76	1.47
50.0	6.60	0.66	76.9	1.49	1.58	0.94

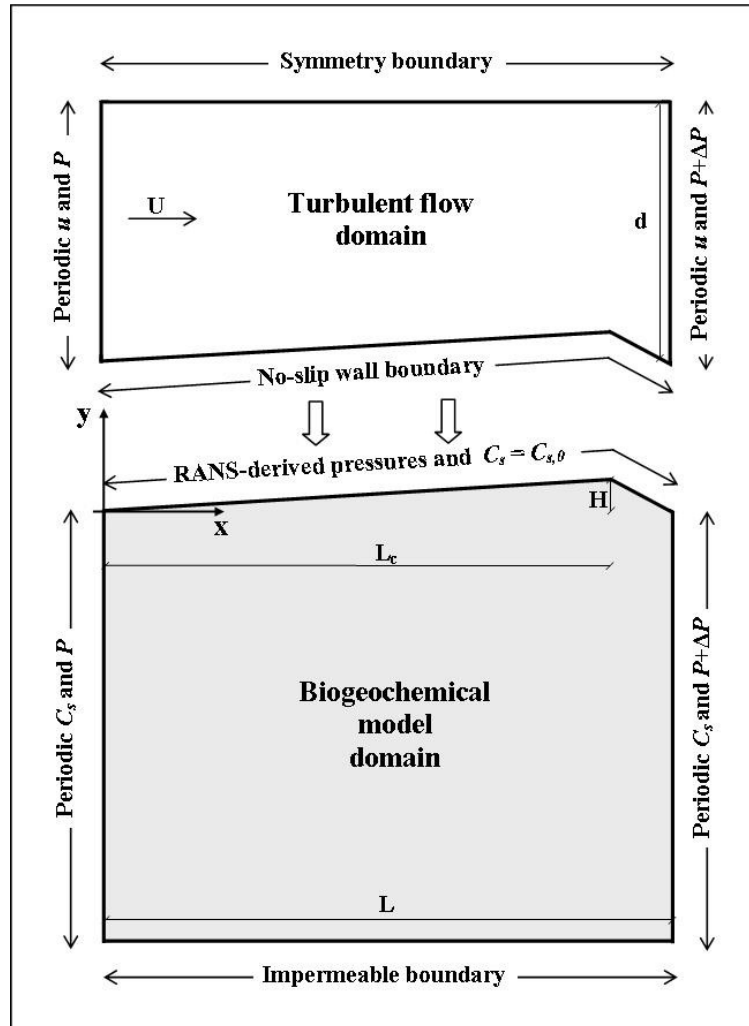


Fig. 1. Modeling scheme. Top part shows the pressure and velocity boundary conditions for the stream water turbulent flow over the streambed; bottom part shows the pressure and concentration boundary conditions for the solute reactive transport in the porous medium. The model domain represents an asymmetrical stream dune of length $L = 1$ m, height $H = 0.075$ m, with the crest shifted on the right ($L_c = 0.9$ m). The streambed depth is 0.8 m. The stream velocity U varies from 0.21 to 0.39 m/s in the simulations.

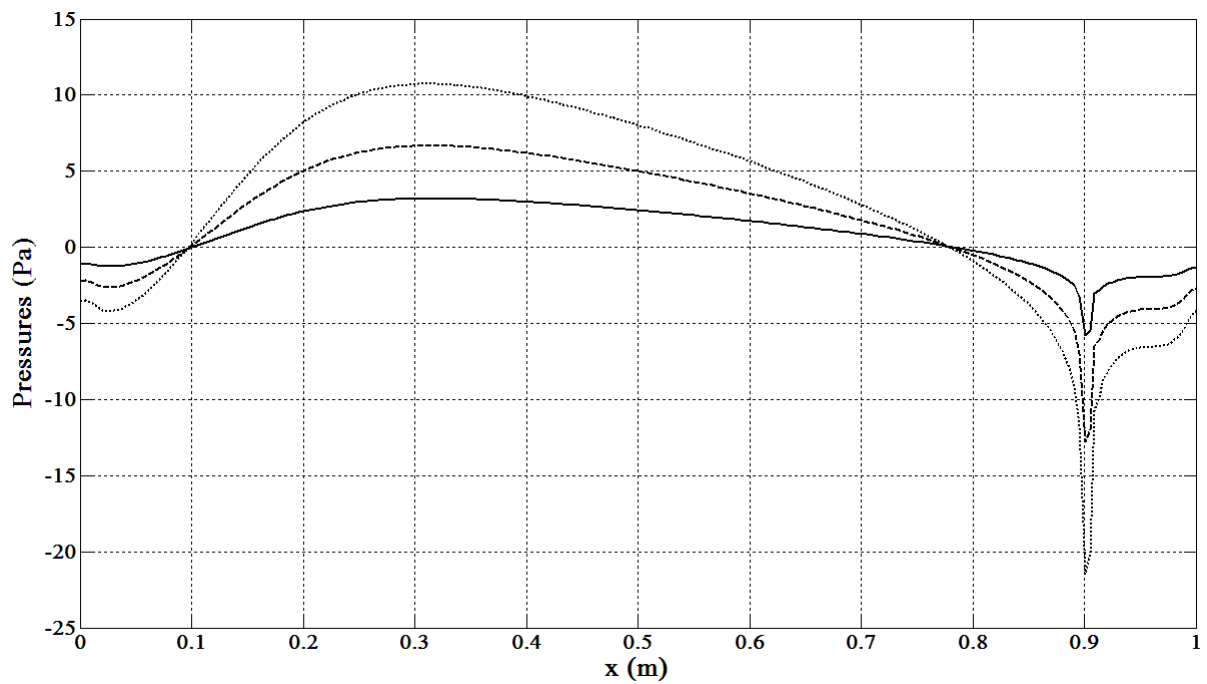


Fig. 2. RANS-derived pressure distributions for stream velocities $U = 0.21$ m/s (solid line), 0.30 m/s (dashed line) and 0.39 m/s (dotted line), corresponding to Reynolds numbers $Re = 106670$, 154120 and 195630 , respectively ($L = 1$ m, $L_c = 0.9$ m, $H = 0.075$ m, $d = 0.5$ m).

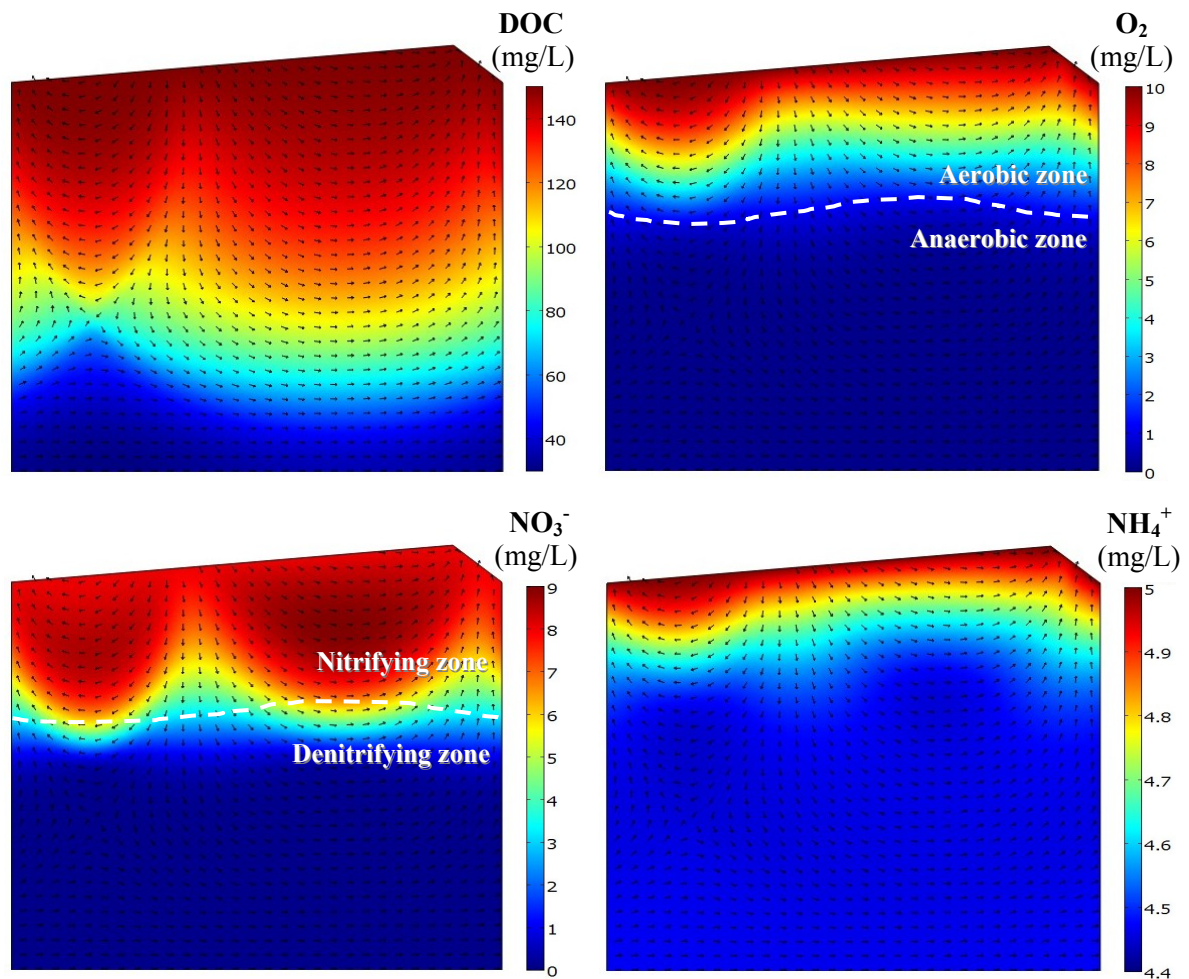


Fig. 3. Solute spatial distribution for the polluted stream (case 1). Stream velocity is $U = 0.33$ m/s, sediment permeability is $\kappa = 10^{-10}$ m², longitudinal dispersivity is $\alpha_L = 3$ mm. DOC reaction rate is $k_{DOC} = 5 \cdot 10^{-6}$ s⁻¹, nitrification rate is $k_n = 5 \cdot 10^{-6}$ L/(mg·s). In-stream concentrations are shown in Table 2. Vectors are only indicative of flow direction.

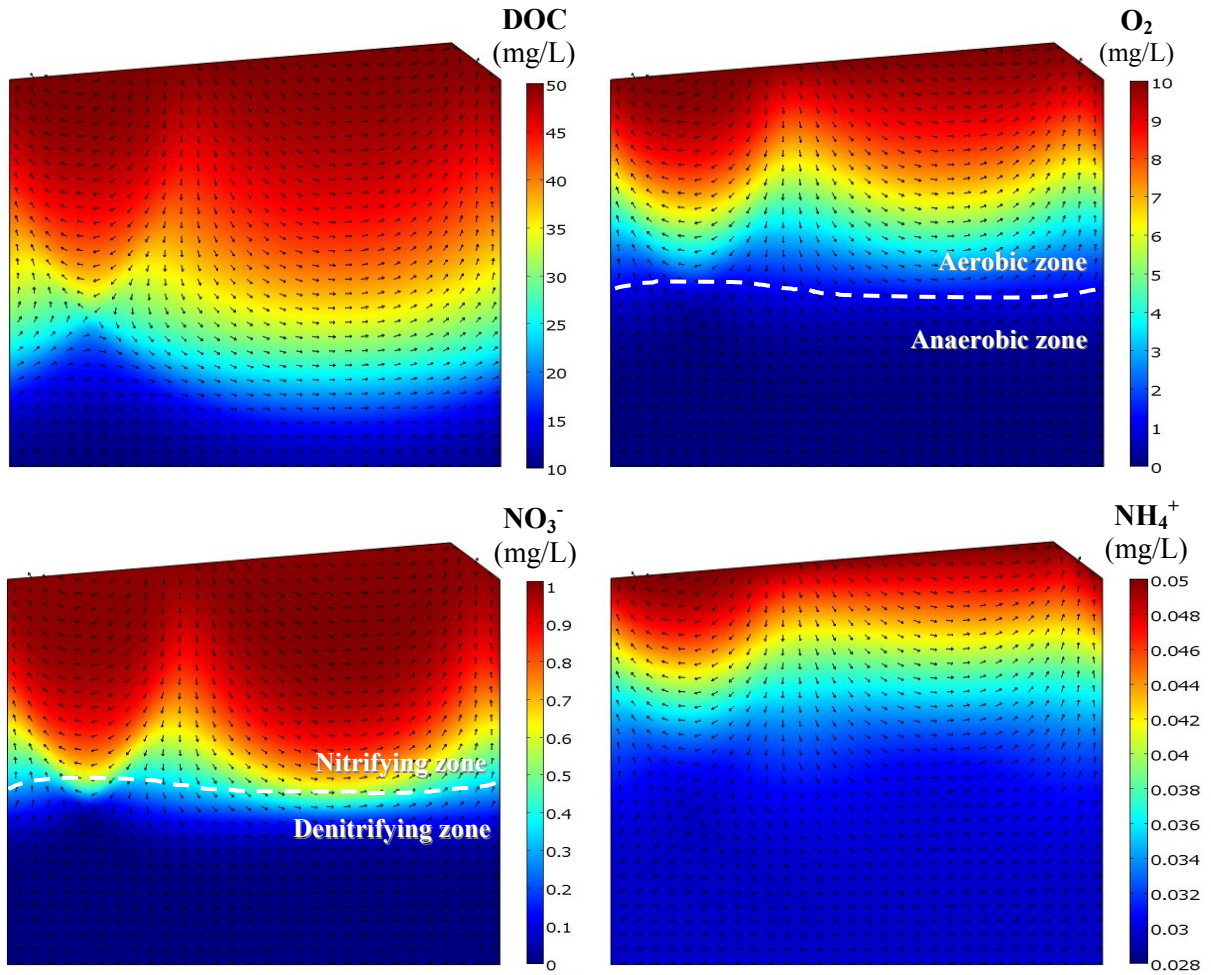


Fig. 4. Solute spatial distribution for the pristine stream with no DOC limitation (case 2). Stream velocity is $U = 0.33$ m/s, sediment permeability is $\kappa = 10^{-10}$ m² and longitudinal dispersivity is $\alpha_L = 3$ mm. DOC reaction rate is $k_{DOC} = 5 \cdot 10^{-6}$ s⁻¹, nitrification rate is $k_n = 5 \cdot 10^{-6}$ L/(mg·s). In-stream concentrations are shown in Table 2. Vectors are indicative of flow direction.

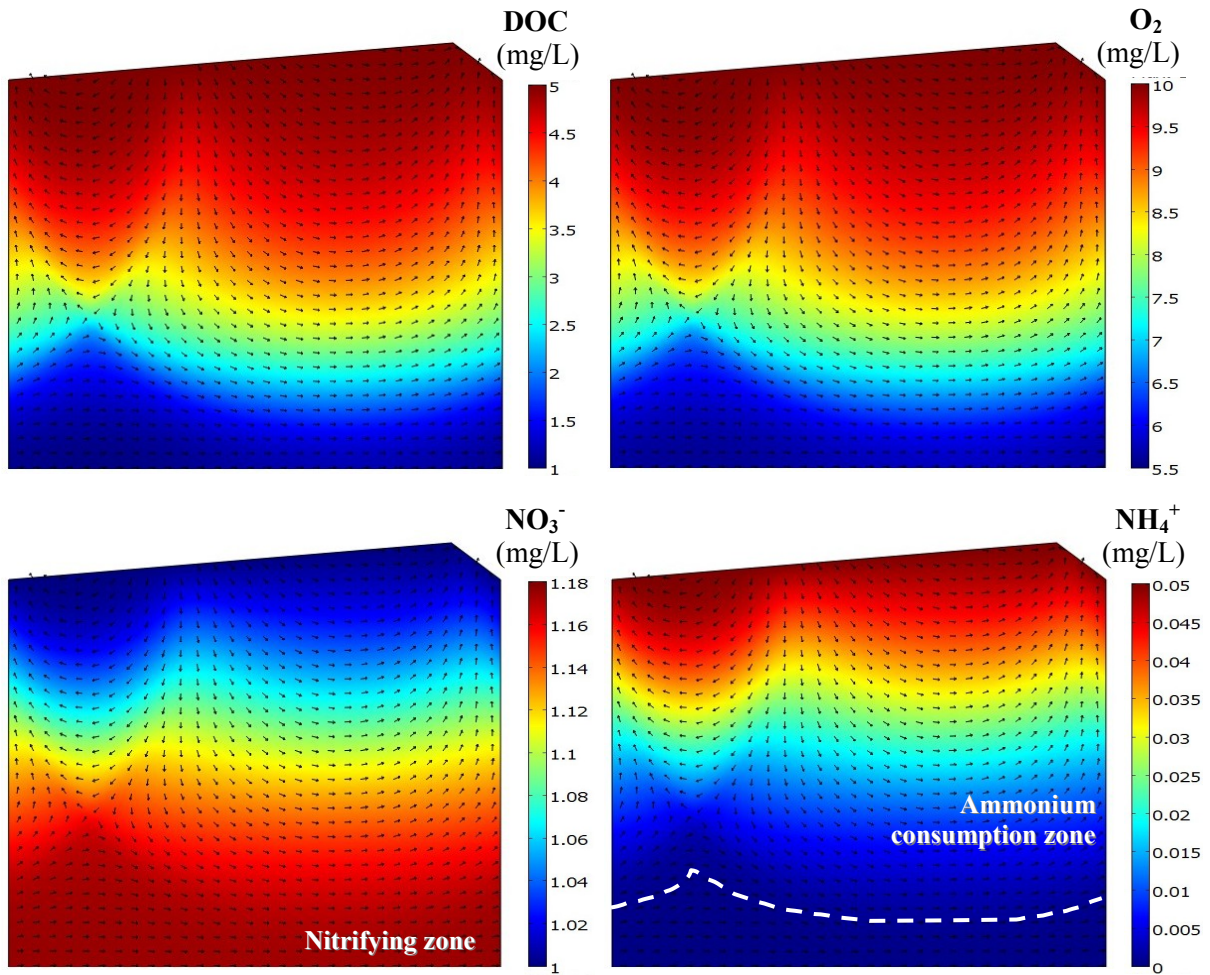


Fig. 5. Solute spatial distribution for the pristine stream with DOC limitation (case 3). Stream velocity is $U = 0.33$ m/s, sediment permeability is $\kappa = 10^{-10}$ m², longitudinal dispersivity is $\alpha_L = 3$ mm. DOC reaction rate is $k_{DOC} = 5 \cdot 10^{-6}$ s⁻¹, nitrification rate is $k_n = 5 \cdot 10^{-6}$ L/(mg·s). In-stream concentrations are shown in Table 2. Vectors are only indicative of flow direction.

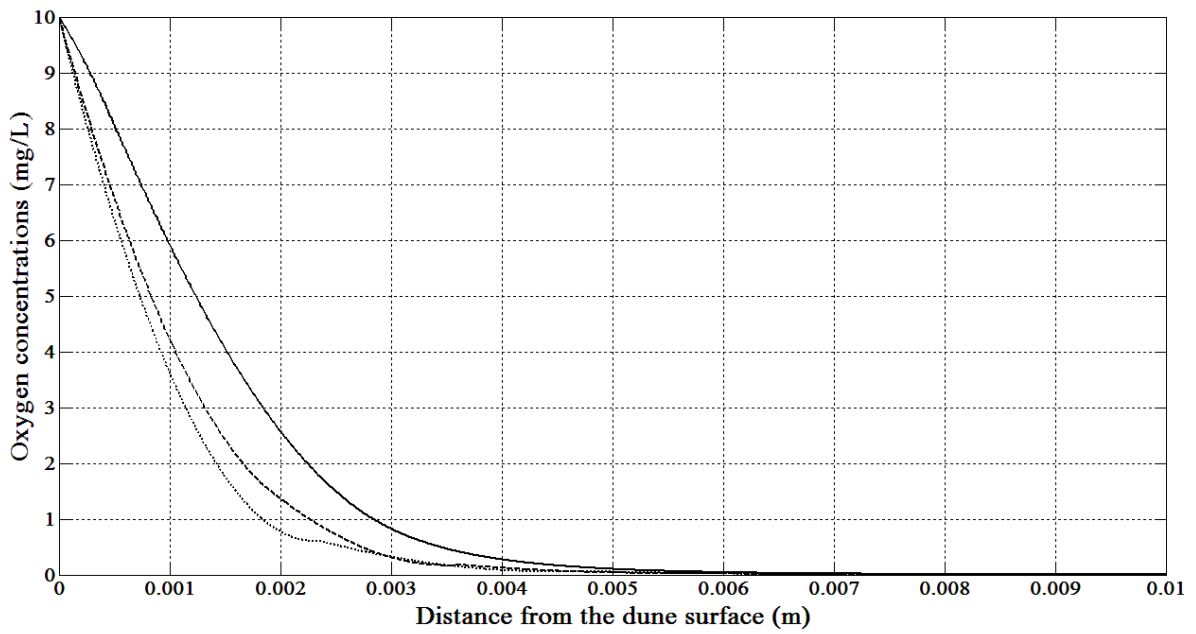


Fig. 6. Oxygen concentrations for case 2, under diffusive conditions, at $x = 0$ m (solid line), $x = 0.5$ m (dashed line) and $x = 0.9$ m (dotted line).

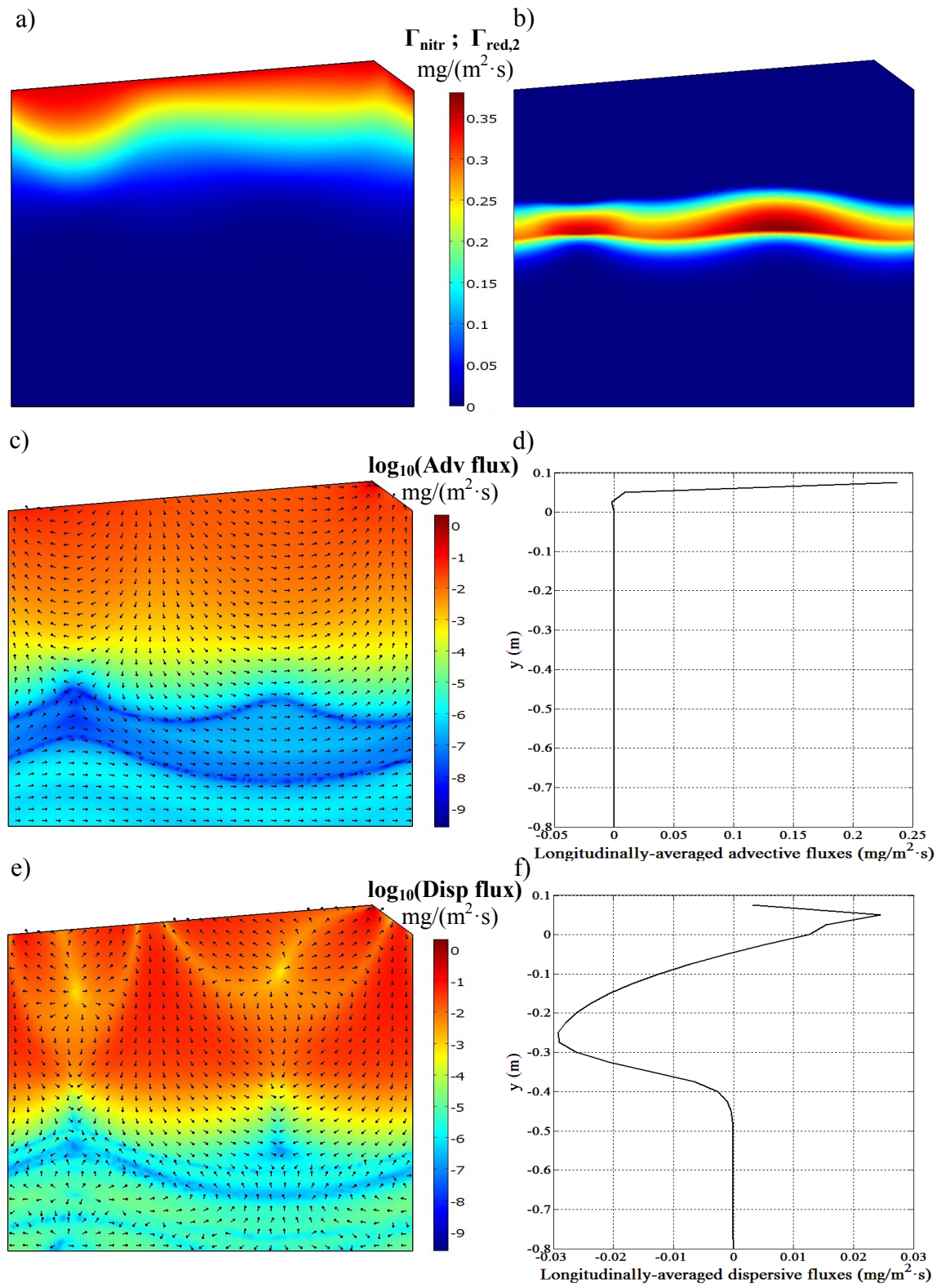


Fig. 7. Nitrification and denitrification rates (Fig. 7a, 7b), logarithmic values and longitudinally-averaged vertical profiles of advective (Fig. 7c, 7d) and dispersive (Fig. 7e, 7f) fluxes of nitrate (case 1). Vectors are only indicative of flux direction.

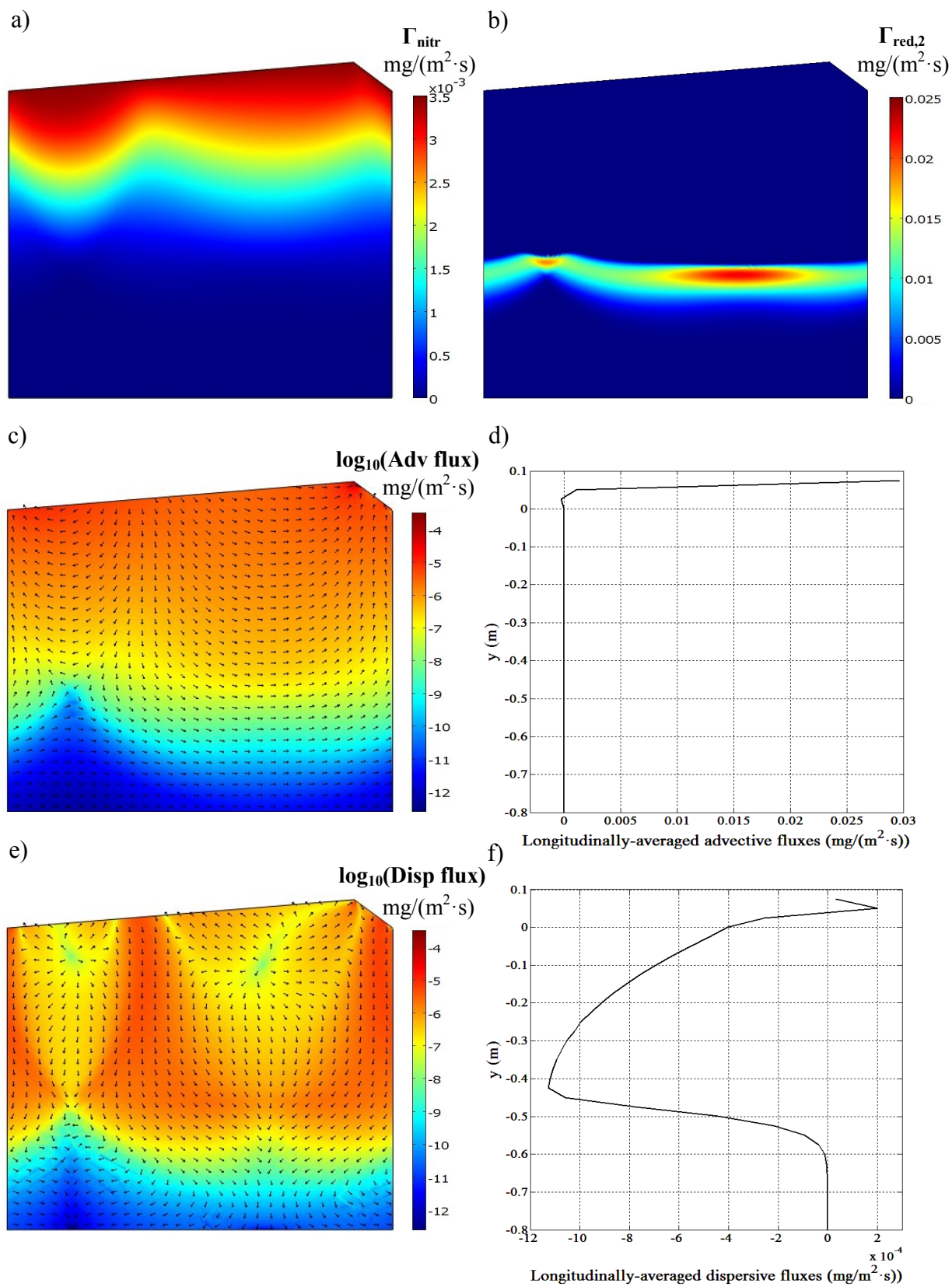


Fig. 8. Nitrification and denitrification rates (Fig. 8a, 8b), logarithmic values and longitudinally-averaged vertical profiles of advective (Fig. 8c, 8d) and dispersive (Fig. 8e, 8f) fluxes of nitrate (case 2). Vectors are only indicative of flux direction.

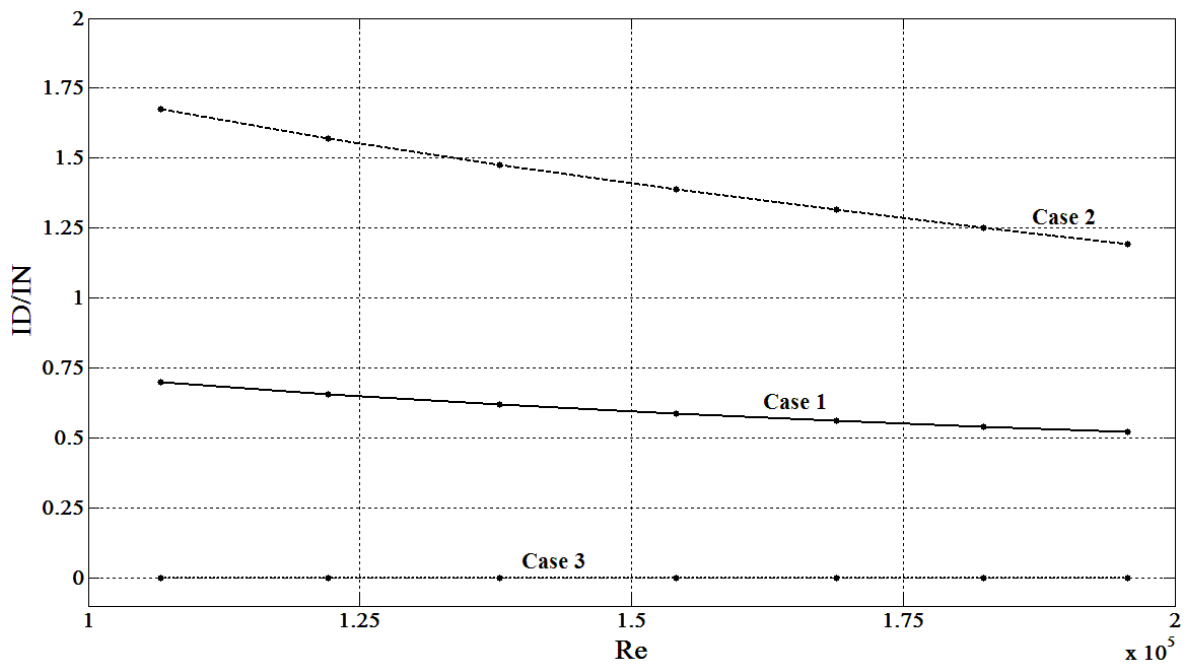


Fig. 9. Ratio of ID to IN rates vs. Reynolds numbers for case 1 (solid line), case 2 (dashed line) and case 3 (dotted line).

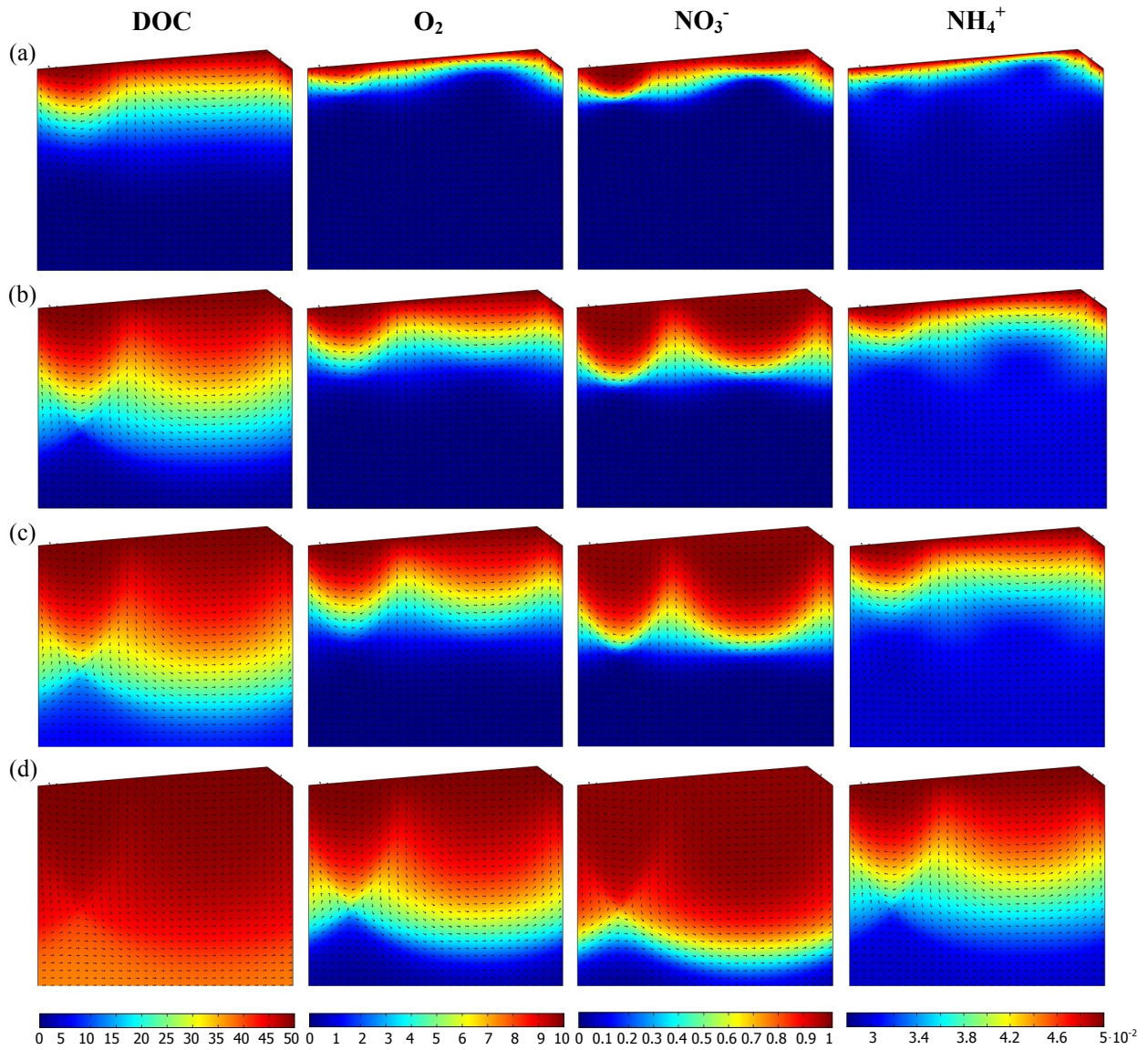


Fig. 10. Solute spatial distributions for case 2 (see Table 2), with stream velocity $U = 0.27$ m/s and sediment permeabilities $\kappa = 10^{-11}$ m² (Fig. 9a), $5 \cdot 10^{-11}$ m² (Fig. 9b), 10^{-10} m² (Fig. 9c), $5 \cdot 10^{-10}$ m² (Fig. 9d). DOC reaction rate is $k_{DOC} = 5 \cdot 10^{-6}$ s⁻¹, nitrification rate is $k_n = 5 \cdot 10^{-6}$ L/(mg·s). All concentrations are expressed in mg/L.