Modélisation du flux de nutriments à l'interface eau-sédiment

Marie Thouvenot, G. Billen, J.Garnier

UMR Sisyphe 7619, UPMC-CNRS, marie.thouvenot@hut.fi

1. Introduction

L'objectif de ce travail, réalisé au cours d'un satge de Master 2 à l'UPMC, est la réalisation d'un modèle numérique biogéochimique capable de prendre en compte la diagénèse du sédiment dans la modélisation de la qualité des eaux.

Actuellement, peu de modèles couplent des modèles benthiques aux modèles pélagiques. Pourtant, les processus prenant place dans le sédiment et dans la colonne d'eau sont interdépendants. Il est important de relier quantitativement les flux de matière particulaire déposés à la surface du sédiment aux flux résultants de nutriments dissous (oxygène, ammonium, nitrates, silice, phosphates…) à travers l'interface eau/sédiment. Ces échanges résultent de conditions physiques et chimiques particulières ainsi que de l'activité microbiologique au sein du sédiment.

Récemment, des progrès considérables ont été réalisés dans la modélisation des processus d'apports de matériel particulaire issus de l'érosion vers les cours d'eau ainsi que des processus de dépôt/érosion de particules. Les modèles de rivière les plus récents (SENECAM (Ruelland and Billen, 2005); CAWACQS (Flipo, 2005)) sont donc à même aujourd'hui d'intégrer une représentation des processus de dépôt temporaire et de remise en suspension du matériel particulaire en fonction de l'hydrologie. Il restait cependant à formaliser les processus diagénétiques proprement dit d'une manière compatible avec cette représentation pour permettre le couplage d'un modèle de transport-réaction dans la colonne d'eau à un modèle de diagénèse dans les sédiments. C'est donc dans cette optique d'intégration du sous-modèle benthique à un modèle générique de qualité des eaux douces que nous avons développé notre propre modèle diagénétique.

Les travaux que nous avons menés au cours de ce stage ont débouché sur la rédaction d'un article en anglais, intitulé « Modelling nutrient exchange at the sediment – water interface of River Systems », à soumettre à la revue Ecological Modelling. Nous avons donc choisi d'articuler le présent mémoire autour du texte de cet article. L'article sera tout d'abord introduit par une revue bibliographique sur les cycles biogéochimiques dans le sédiment et sur les modèles diagénétiques. On reprendra ensuite les bases du sous-modèle benthique développé lors de ce travail. Enfin, l'article, qui présentera les résultats de l'utilisation de ce modèle dans trois études de cas tirées de la littérature, sera

inclus in extenso. Une conclusion en français permettra de présenter les perspectives sur lesquelles débouchent notre travail.

2. Cadre conceptuel

L'intérêt porté au transport et à la réaction des substances dans le sédiment (diagénèse) est apparu dans les années 1980 (Lerman, 1978; Berner, 1980). La diagénèse du sédiment regroupe l'ensemble des processus affectant un dépôt de sédiments et le transformant progressivement ce dépôt en roche sédimentaire (du grec dia, à travers, et genêsis, formation). Les processus mis en place dépendent de la nature chimique du sédiment, du taux de sédimentation contrôlant l'enfouissement, etc. On s'intéresse ici particulièrement à la diagénèse précoce du sédiment qui est réalisée en surface du sédiment là où l'activité biologique est importante. Lors de la diagenèse, le milieu devient plus acide et plus réducteur. Les oxydants sont réduits progressivement pour permettre l'oxydation de la matière organique. On assiste à un appauvrissement successif des oxydants, des plus oxydants vers les moins oxydants, oxygène, oxyde de manganèse, nitrate, fer ferrique, sulfate.

L'utilisation de modèles mathématiques est indispensable à la compréhension des phénomènes diagénétiques car peu de données sont disponibles (flux à l'interface eau/sédiment et profils de concentration dans le sédiment) et de nombreux processus interagissent (Boudreau, 1997). La diagénèse de la matière organique et des nutriments reste un problème important de la recherche géochimique. Il y a un besoin fondamental de comprendre quantitativement les processus qui contrôlent cette diagénèse pour être capable de prédire leur réponse à une échelle globale et locale dans un système sédimentaire (Boudreau, 1996). Les composés retournant à la colonne d'eau après diagénèse sont fondamentalement différents de ceux déposés suite aux réactions d'oxydo-réduction, de dissolution, ou d'adsorption/désorption qu'ils subissent. Beaucoup de ces processus prennent place à des profondeurs définies dans le sédiment, où les conditions biogéochimiques sont favorables. Les modèles diagénétiques distribués du sédiment permettent la représentation de ces processus biogéochimiques et relient ainsi le flux de déposition de matières particulaires au flux résultant de nutriments et d'oxygène à l'interface eau/sédiment.

Les modèles diagénétiques développés depuis les années 1980 se sont essentiellement intéressés aux milieux lacustres et marins, la situation étant beaucoup plus complexe en rivière. Dans les secteurs à courant lent on peut retrouver des situations de dépôt sédimentaire similaires à celles des lacs, et dans les zones à courant rapide, des situations d'érosion nette, où seul un biofilm, par ailleurs potentiellement siège d'une production algale benthique, se développe parfois directement sur un substrat rocheux. Dans tous les cas la variabilité temporelle et spatiale des situations est très grande. Tout le spectre de ces situations devrait pouvoir être pris en compte par le modèle que nous cherchons à construire.

3. Le modèle diagénétique

3.1. Données expérimentales

Dans l'étude expérimentale in-situ de la biogéochimie du sédiment et des flux échangés à son interface, le problème majeur est d'éviter toute perturbation du sédiment lors du prélèvement. Pour cela, plusieurs techniques ont été développées.

3.1.1 Les mesures de flux

Les échanges entre le sédiment et la colonne d'eau sus-jacente peuvent être mesurés à l'aide de chambres benthiques. Ces chambres sont utilisées depuis les années 1960. Elles sont placées sur le sédiment et à intervalle de temps des échantillons d'eau sont prélevés dans la chambre à l'aide d'une seringue (Figure 2 et Photographie 2). L'analyse des nutriments dans l'eau permet de connaître l'évolution dans le temps des concentrations et ainsi de déterminer les échanges entre l'eau et le sédiment. Des sondes peuvent être ajoutées au dispositif afin de mesurer l'évolution de l'oxygène par exemple.

Figure 1:Chambre benthique (Sanchez, 1997).

Photographie 1 : Cloches benthiques utilisées lors de lacampagne de prélèvements à Melarchez en Avril 2005

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3.1.2 Les mesures de concentration dans le sédiment

D'autres techniques permettent de mesurer la concentration de l'oxygène et des nutriments dans le sédiment par des méthodes plus ou moins invasives : sondes électrochimiques, sondes optiques et certaines techniques d'échantillonnage de l'eau interstitielle (Viollier et al., 2003).

Les sondes électrochimiques permettent une étude du sédiment minimisant les problèmes de mélange, car le sédiment n'est pas prélevé mais analysé sur place. Toutefois, une analyse sur le terrain peut s'avérer moins fiable. Les sondes optiques ont un autre avantage qui est de ne pas consommer l'électrolyte (par exemple oxygène) lors de son analyse. Enfin, des techniques d'échantillonnage du sédiment pour récupérer l'eau interstitielle piégée sont utilisées pour permettre l'analyse de composés ne pouvant être analysés autrement. Des méthodes de prélèvement, de séparation du sédiment en couche et de filtration de l'eau interstitielle ont été utilisées dans le passé. A présent, les gels de polyacrilamide permettent un échantillonnage de l'eau interstitielle sans perturbation du milieu. La résolution des couches est de 0.1 à 10 mm de profondeur ce qui permet une analyse détaillée des profils de concentration dans le sédiment. Toutefois, cette technique rend l'analyse des échantillons difficile à cause du volume restreint collecté.

3.2.   Les hypothèses de travail

Les nécessités du couplage du sous-modèle benthique au modèle générique de qualité des eaux nous ont amenés à une représentation du sédiment en deux couches. La couche supérieure représente un sédiment fluide, érodable et pouvant permettre la croissance d'algues benthiques. La couche inférieure, compactée, est pour sa part non érodable et ne peut accueillir de développement algal. Cette couche est alimentée par la compaction de la couche supérieure. Les 2 couches sont caractérisées par des porosités différentes, la couche supérieure étant maintenue plus fluide par une action physique et/ou biologique. Suite à la collecte de différentes colonnes de sédiments sur le terrain (campagne de Melarchez dans le bassin de l'Orgeval en avril 2004), nous avons observé la présence d'une couche de sédiment plus fluide à la surface sur une profondeur de 0 à 1 cm (Figure 2 et Photographie 2). Ces observations sont à rapprocher de celles de Vanderborght et al., 1977) sur les sédiments côtiers de la mer du Nord où la porosité superficielle (90%) est bien supérieure à la porosité profonde (60%), et à peu près homogène sur une épaisseur de 2-3 cm environ.
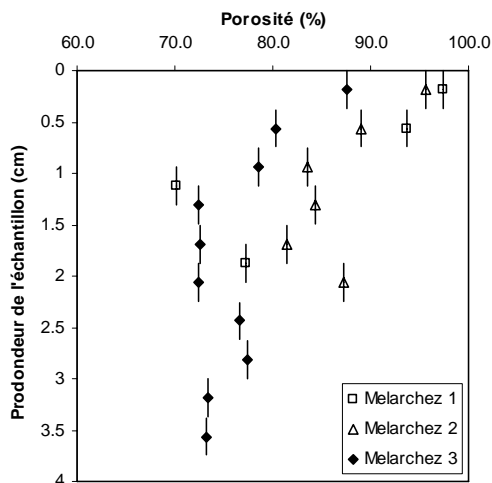

Figure 2: Profil vertical de la porosité du sédiment de plusieurs échantillons collectés à Melarchez (bassin de l'Orgeval) en avril 2005

Photographie 2: Échantillon de sédiment prélevé à Loge en mai 2005.

On fera l'hypothèse que la couche supérieure, fluide, est bien mélangée et donc uniforme en terme de concentration de toutes les variables particulaires sur toute sa profondeur. Dans le modèle de rivière, c'est le modèle numérique, représentant les processus d'érosion, sédimentation et réactions, qui fixe, à chaque pas de temps, cette concentration uniforme, utilisée comme donnée d'entrée dans le modèle benthique. Le modèle benthique calcule alors les profils stationnaires de la concentration des variables dissoutes en fonction de la profondeur dans les 2 couches sédimentaires et en déduit la valeur des flux diffusifs à travers l'interface sédiment-eau. L'hypothèse de stationnarité a été choisie afin de permettre une résolution analytique des équations diagénétiques et de leur intégration sur la profondeur, permettant de s'affranchir de la lourdeur d'un calcul numérique dans lequel chacune des variables devrait être indicée par autant de couches élémentaires sur la profondeur qu'en exigerait un calcul numérique précis. Le pas de temps de calcul du modèle benthique peut être plus long que celui du modèle pélagique, le premier calculant alors les flux correspondants à la moyenne intégrée sur son pas de temps des conditions de déposition. Les équations diagénétiques résolues dans ce modèle comportent un terme de transport par diffusion (Loi de Fick) et par convection (compaction) et un terme de réaction tels que la dissolution, l'adsorption/désorption et l'oxydo-réduction. La formulation des cinétiques se veut totalement générique et s'applique donc aussi bien aux petits cours d'eau où la profondeur de la colonne d'eau est peu importante (ordres 1 à 4-5), qu'aux grands cours d'eau et aux lacs où le temps de résidence de l'eau est long et la déposition importante.

On fera l'hypothèse dans le sous-modèle benthique de l'universalité des processus fondamentaux que sont la dégradation bactérienne de la matière organique, la nitrification, la dénitrification, la dissolution de matières solides etc. qui obéissent aux mêmes contrôles cinétiques et ont lieu dans tous les écosystèmes aquatiques. Les paramètres utilisés dans le modèle benthique sont donc essentiellement les mêmes que dans le modèle principal de la colonne d'eau. On fait donc l'hypothèse que la variabilité du fonctionnement écologique s'explique par la diversité des contraintes externes (lumière, température, facteurs inhibiteurs (i.e. oxygène pour la dénitrification), apports externes etc.). Alors que la température régit les processus biologiques (nitrification, dégradation de la matière organique, production primaire, dissolution, adsorption/désorption), la lumière influence la production primaire des algues benthiques et est prise en compte dans les données de croissance algale. Le périphyton est représenté en surface du sédiment uniquement.

Les équations diagénétiques utilisées dans le modèle et leur résolution sont explicitées en annexe 1 de l'article.

3.3.   Présentation de l'interface Visual Basic

Une interface utilisateur du sous-modèle benthique a été développée sous Visual basic 6.0 (Figure 3). Les données d'entrées du modèle et les paramètres peuvent être modifiés au sein de l'interface. Les données observées peuvent être comparées aux résultats du modèle grâce à l'ouverture d'un fichier texte rassemblant ces données. Les graphiques peuvent être exportés soit sous forme de fichier Excel, soit directement sous un format image. Enfin, les données d'entrées ainsi que les paramètres utilisés pour la modélisation peuvent être sauvegardés sous forme de fichier texte.
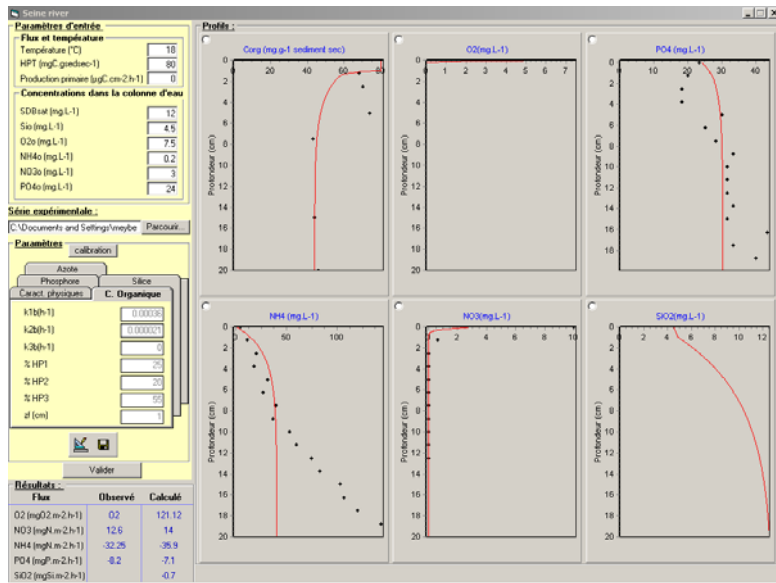
Figure 3 : Interface utilisateur du sous-modèle benthique

4. Résultats

4   Résultats

Les résultats sont présentés ci-dessous au sein de l'article « Modelling nutrient exchange at the sediment – water interface of a River Continuum ».

Modelling nutrient exchange at the sediment – water interface of River Systems

Marie Thouvenot [1,2], Gilles Billen [2], Josette Garnier [2] and Nathalie Sanchez [2]

1- Water Resources Engineering, Helsinki University of Technology, P.O.Box 5200, FIN-0215 HUT, Finland.
2- U.M.R. 7619 Sisyphe, University Pierre et Marie Curie, Boite 123, 4 place Jussieu, Tour 56, Couloir 46-56,3°étage, 75252 PARIS Cedex 05, France

Abstract

In-stream benthic processes can play a significant role on the water quality of overlying waters flowing through a river network. In order to better understand and quantify the fate of nutrients (nitrogen, phosphorus and silica) during their travel to the river continuum, a deterministic benthic sub-model was developed with the purpose of being connected to a drainage network model. This benthic sub-model resolves the differential equations representing early diagenesis in the sediment, linking the sedimentation rate of organic matter at the surface of the sediment to the resulting flux of nutrients at the sediment-water interface. The model has been developed for conditions where sedimentation prevails as well as for situations where net erosion prevents the built-up of a significant sediment layer and where only a biofilm can develop, attached to solid substrates. The benthic model was tested independently of the main water column biological-hydrological model to which it is intended to be coupled. For this, three case studies were chosen from the literature representing various sedimentation/erosion conditions: the water storage basin of Mery s/Oise (France), the 8th order river Seine (France) and the headwater stream Orneau (Belgium). The general benthic model has been validated for ammonium, nitrate, oxygen and phosphorus flux across the sediment-water interface, while silica could not be fully tested due to a lack of data. The capability of the model to correctly predict the observed nutrients profiles within the sediment was also validated for organic carbon, ammonium and phosphorus. A sensitivity analysis illustrated the complexity of the interacting reactions driving each variable, and justifies the usefulness of the model as a tool for understanding and predicting the behaviour of the benthic compartment of river systems.

Introduction

In an attempt to quantify and understand the fate of nutrients from catchment based sources during their transfer through the river continuum to downstream freshwater or marine water bodies, dynamical simulation models of whole river systems have proven very useful (Sferratore *et al*., submitted; Whitehead *et al*., 1998; Whitehead *et al*., 1998; Krysanova and Becker, 1999; Smitz *et al*., 1999; Everbecq *et al*., 2001) and have reach a large degree of genericity. The challenge of this kind of models is to combine a mechanistic representation of the complex biogeochemical interactions characterising aquatic systems with a description of

the hydrology of the entire drainage network. Whereas many progress have been achieved in the representation of planktonic processes at this scale, benthic processes are often still very simplistically represented. Yet, benthic processes play a very significant role in nutrient retention and elimination during their downstream travel through river continuums (Birgand, 2000; Seitzinger *et al.*, 2002) and benthic biofilms in shallow rivers and streams can be the site of a more significant primary and secondary production than the water column (Flipo *et al.*, 2004).

Deterministic models describing benthic nutrient dynamics were up to now mainly developed for marine or lake sediments. Diagenetic models were first developed for representing the long term fate of organic material after burial, but also to calculate the resulting flux of remineralised nutrient diffusing across the sediment-water interface, provided stationary conditions are assumed (Lerman, 1978; Berner, 1980; Billen and Lancelot, 1988; Rabouille and Gaillard, 1991; Soetaert *et al.*, 1996). Only a few of these models deal with more than three compounds at a time and even fewer consider more than one electron acceptor for organic matter degradation (Rabouille and Gaillard, 1991; Jahnke, 1998). A few non-stationary models of coupled water column - sediments systems have been proposed, calculating the fate of all state variables in a number of interacting horizontal layers of sediments (Boudreau, 1996), but this kind of models requires considerable computational capacities.

River systems, including their hydrological annexes (like ponds, reservoirs, abandoned meanders, etc) are characterized by a succession, both in space and time, of slow and fast flowing sectors so that conditions of deposition and erosion of particulate material can alternate very rapidly. Modelling solid transport, erosion and deposition within river system has made serious progress during the last decades (Martin, 2001; Celik and Rodi, 1991) and biogeochemical river system models now integrate particle transport equations which allow to correctly simulate areas of particulate material deposition or erosion in a drainage network (Cerdan *et al.*, 2003; Even *et al.*, 2004). Many such models thus consider benthic stocks of deposited material as state variables in the same way as they do for planktonic variables. The question we wish to address in this paper is how to connect a model of diagenetic nutrient transformation to such model of water column processes (including particles transport and deposition) to realistically and generically represent benthic processes at the scale of an entire drainage network.

We will first present the hypothesis leading to the formulation and the resolution of the equations representing benthic transformations of organic matter, oxygen and nutrients (N, P, Si). The structure of the kinetic relationships adopted and the value of the corresponding parameters chosen will be discussed on the basis of literature. We will then apply the model to three situations characteristic of the diversity of conditions existing within river systems, for which we could assemble, either from the literature or from our own previous work, a sufficient data base of experimental observations to document both nutrient fluxes across the water-sediment interface and the vertical distribution of chemical variables in the sedimentary layers. These situations include (i) the storage water basin of Mery S/Oise; (ii) the lower course of the regulated Seine river, downstream from Paris, where, under summer low flow conditions, considerable sediment deposition occurs, which are re-eroded during floods; (iii) the situation of small headwater streams where sectors of net deposition alternate with sectors of net erosion where only a thin biofilm develops on hard substrates. In each of these three situations we will show that our generic model is able to correctly predict the available observations.

Model description

General hypothesis

We will consider that our benthic sub-model is to be connected to a drainage network model (here referred to as the 'main model') dealing with suspended solid transport and deposition. The main model is supposed to numerically calculate, at a suitable time scale, not only all water quality variables in the planktonic phase, but also the non-permanent build up and destruction of benthic particulate pools. The process of benthic algal growth and the cumulative establishment of a stock of benthic algal biomass are also assumed to be dealt with by the drainage network model. The function of our benthic sub-model is therefore just to calculate the consequences of this imposed dynamics in term of fluxes of dissolved species between the water column and the sedimentary phase.

As the main objective of this benthic sub-model is to address nutrients cycles at the sediment-water interface, only the vertical dimension is considered. Vanderborght et al. (1977) related porosity profiles in the sediment to mass transfer coefficient as a function of depth. Based on this approach, in each cell of the main model (typically a short river stretch), our sub-model considers two layers of sedimentary material: the upper layer represents freshly deposited, uncompacted material and includes the biofilm; the lower layer, which might be absent in the case of a rocky bottom, represents consolidated sediments. The porosity (ϕ) of both layers differs from each other, the upper layer being subject to turbulence of the overlying water and bioturbation. The effect of turbulence can be increased by biological processes like bioturbation that will maintain a higher porosity in the upper layer. The porosity is assumed constant vertically within each layer.

The main model calculates the depth of the upper layer and the concentration of all particulate variables (organic material, particulate inorganic phosphorus, non living benthic biogenic silica, benthic diatoms), the vertical distribution of which is assumed uniform, except for algal biomass which is considered to be entirely distributed on the top surface. The benthic sub-model thus uses these as forcing variables to calculate (i) the distribution of particulate variables in the lower, compacted, sediment layer; (ii) the distribution of dissolved variables in the two sedimentary layers; and (iii) the resulting fluxes of dissolved species across the water-sediment interface. Only the latter result is used in turn by the main model.

In order to allow the analytical resolution of most of the dynamical equations representing sedimentary diagenesis in the benthic sub-model, steady state conditions will be assumed. Note that the time step of the benthic sub-model is not necessarily identical with that of the main model, so that the former can calculate the sediment-water fluxes resulting from the integrated sedimentary dynamics provided by the latter.

Physical processes

In the benthic sub-model, particulate and dissolved matter are affected by physical and biological processes that can be represented by either diffusion or convection (depositional burial, compaction, water flow, bioturbation) according to Berner (1980).

Convective flux represents the advection or compaction of the sediment to deeper layers. Compaction and advection can be assimilated to a loss of water from a sediment layer (Berner, 1980). The particulate matter is affected by compaction (ω) while advection of

porewater (u) is considered smaller due to extraction of water from the sediment. The corresponding equations are:

$$\frac{\partial C_s}{\partial t} = -\omega \cdot \frac{\partial C_s}{\partial z}$$ (1)

where Cs is the concentration of any solid component ($\mu g.cm^{-3}$); ω is the compaction rate ($cm.h^{-1}$)

$$\frac{\partial C_i}{\partial t} = -u \cdot \frac{\partial C_i}{\partial z}$$ (2)

where Ci is the concentration of any dissolved component ($\mu g.cm^{-3}$); u the advection rate ($cm.h^{-1}$), u = (ϕ_2/ϕ_1)* ω.

Diffusion represents the result of the random motion of particles. In our model we simulate molecular diffusion and local bioturbation using Fick's first law of diffusion for dissolved matter only (Boudreau, 1997). Meiofaunal populations inhabit the benthic zone and enhance the transport rates of solutes due to increased porosity (Aller and Aller, 1992). Hence, we model bioturbation by differentiating porosity and diffusion coefficient between the two layers of sediment. We neglect macrofaunal populations and associated irrigation process. For dissolved species, diffusive fluxes through the sediment are calculated from the chemical gradients of their porewater concentration profiles assuming steady-state conditions and using Fick's first law of diffusion:

$$\frac{\partial C_i}{\partial t} = D \cdot \frac{\partial^2 C_i}{\partial z^2}$$

where D is the diffusion coefficient ($cm^2.h^{-1}$).

The diffusion coefficients of each layer differ due to higher turbulence in the surface layer than in the compacted layer of the sediment. In the compacted layer, we use a coefficient of molecular diffusion varying between 0.035 $cm^2.h^{-1}$ to 0.07 $cm^2.h^{-1}$ depending on the temperature (Li and Gregory, 1974); while the apparent diffusion coefficient at the sediment-water interface is increased to values in a range of 0.1 $cm^2.h^{-1}$ to 6 $cm^2.h^{-1}$ (Billen et al., 1989; Sanchez, 1997).

Noting R the rate of all other chemical and biological processes affecting the concentration of particulate and dissolved matter in the sediment, we can now write the general diagenetic equation for particulate and dissolved components respectively:

$$\frac{\partial C_s}{\partial t} = -\omega \cdot \frac{\partial C_s}{\partial z} \pm R$$

$$\frac{\partial C_i}{\partial t} = D \cdot \frac{\partial^2 C_i}{\partial z^2} - u \cdot \frac{\partial C_i}{\partial z} \pm R$$

These general diagenetic equations have been applied for each layer of sediment (fluid and compacted) and each variable. Moreover, for oxygen, ammonium and nitrate, two sub-layers should be considered to represent oxic and anoxic layers (see below). The porosity is constant over each layer of sediment (fluid and compacted). The change in porosity is taken into account in the boundary conditions as the concentrations of solid and dissolved matter are expressed in $\mu g.cm^{-3}$ of total sediment. At the interface of the fluid and compacted layer, the boundary conditions can be written as:

For particulate matter: $\dfrac{\left(C_{Sf}\right)_{zf}}{\left(1-\phi_f\right)} = \dfrac{\left(C_{Sc}\right)_{zf}}{\left(1-\phi_c\right)}$

For dissolved matter: $\dfrac{\left(C_{if}\right)_{zf}}{\phi_f} = \dfrac{\left(C_{ic}\right)_{zf}}{\phi_c}$

All the diagenetic equations used for the development of the benthic sub-model are expressed in Appendix 1 with their solutions. Two cases have been described; one general case where deposition is predominant compare to erosion, so that the sediment layer is deep enough to be represented as two layers of sediment (fluid and compacted). Another case, more specific, has been added for modelling the situation corresponding to fast flowing stretches of rivers, where no accumulation of sediment can be observed but an attached benthic biofilm is growing on a rocky bottom, trapping some sediments within an algal mat. In this case, only the fluid layer of sediment is considered, overlaying a solid substrate.

Biogeochemical processes

The kinetic expression of the biogeochemical reaction terms used in the diagenetic equations are presented below for each variables. The benthic sub-model takes into account the reactions of organic matter degradation, that releases ammonium and phosphate and consumes oxygen and nitrate, nitrification, phosphate and ammonium adsorption onto the mineral matter and silica dissolution. The reactions considered in the model with their kinetic parameters gathered from the literature are summarised in Table 1. The kinetics of the major processes involved in the ecological functioning are mostly derived from experimental data in order to reduce the problem of equifinality or non-uniqueness described by Beven (2000). The problem of equifinality describes that more than one set of parameter values can give acceptable predictions of the observed data; by narrowing the range of parameter values, we are narrowing down the problem of equifinalty. All biogeochemical processes taken into account in the benthic sub-model and discussed below are summarised in Figure 1.
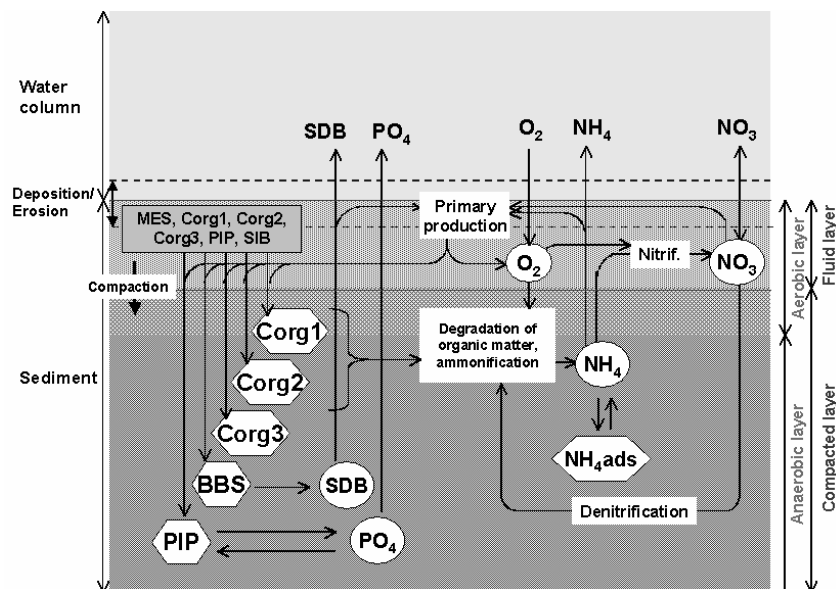
Figure 1: Reactions represented in the benthic sub-model; Corg 1, 2 and 3 refers to the three classes of organic carbon, SDB: Dissolved biogenic silica; BBS: Biogenic silica; PIP: particulate inorganic phosphorus; PO_4: Dissolved inorganic phosphorus; O_2: Dissolved Oxygen; NH_4: dissolved ammonium; NH_{4ads}: Ammonium adsorbed onto the sediment; NO_3: Dissolved nitrate; nitrif.: nitrification process; Primary production

Primary production

Primary production (PP, $mgC.cm^{-3}.h^{-1}$) decreases exponentially with depth due to the decreasing light penetrating the sediments. It follows the relationship:

$$PP(z) = \delta.IPP \cdot e^{-\delta \cdot z}$$

where, IPP is the integrated value of primary production ($\mu gC.cm^{-2}.h^{-1}$), and δ an attenuation coefficient (cm^{-1}).

Organic carbon

We use the "multi Gs- first-order kinetics" approach to model organic material in the benthic sub-model (Jorgensen, 1979, Berner, 1980, Billen and Lancelot, 1988). Three classes of organic material (1 to 3) are considered to represent the differing biodegradability of the various organic compounds.

$Corg = \Sigma_i Corg_i$

$$\frac{\partial Corg_i}{\partial t} = -ki \cdot Corg_i$$

ki= first order biodegradation constant for organic carbon class i (h^{-1}).

In agreement with the work of Westrich and Berner (1984), Kristensen and Blackburn (1987) and our own unpublished results, we assume that biodegradation of each class of organic carbon occurs at the same rate in aerobiosis and in anaerobiosis.

Oxygen

Beside diffusion from the overlying water, oxygen in the sediment is affected by a production linked to primary production on the top of the surface layer (if light penetrates through the water column) and by consumption linked to organic matter biodegradation and ammonium oxidation through nitrification. All these processes ceases below the point where oxygen concentration reach zero, thus defining the depth of the oxic layer (z_n). This layer can be shallower than the fluid layer (z_f) ($z_n < z_f$) or can penetrate deeper and reach the compacted layer ($z_n > z_f$). The depth of oxygen penetration into the sediment affects the simulation of ammonium and nitrate as both variables closely depends on aerobic or anaerobic conditions.

Ammonium

Ammonium is produced by the organic material degradation and can be oxidised into nitrate or consumed by algae for their growth. The nitrification zone is limited to the oxygenated layer of sediments as assumed by Billen and Lancelot (1988). It is reversibly adsorbed on particulate material, according to first order equilibrium, as proposed by Lerman (1978).

Nitrate

Nitrate is produced by nitrification of ammonium in the oxic layer and can be reduced to gaseous nitrogen (denitrification) within the anoxic layer. In the latter case, nitrate replaces oxygen as an electron acceptor and is denitrified at the rate of organic matter biodegradation. For simplification, we considered a first order denitrification rate, and we related the value of the first order kinetic constant to the rate of organic matter degradation at the bottom of the oxic layer according to the relationship:

$$denit = \frac{\lambda \cdot \left(\sum_i kib \cdot Corgi \right)}{2 \cdot Km_{NO3}}$$

where λ is a stoechiometric coefficient relating nitrate consumption to organic matter degradation; Km_{NO3} represents the Michaelis constant with respect to nitrate concentration for denitrification (between 25-50 µM or higher according to Billen and Lancelot (1988).

Phosphorus

Inorganic phosphorus in sediments is consumed by benthic algal growth and produced by the mineralization of organic matter. Total inorganic phosphorus (PIT) in sediments occurs both under dissolved and adsorbed, more or less readily exchangeable, forms. Dissolved phosphorus is reversibly absorbed onto the sediment into a particulate form that can be represented as a first order equilibrium like for ammonium:

$$\begin{cases} PIP = K_{PO4} \cdot PO_4 \\ PIT = (1 + K_{PO4}) \cdot PO_4 \end{cases}$$

Silica

Silica is present in the sediment as solid biogenic silica and dissolved silica (SiO_2). Dissolved silica is taken up by benthic diatoms as it enters the composition of their frustule (Garnier *et al.* (2002). Besides, biogenic silica follows a dissolution process that is function of the distance of dissolved silica concentration in the sediment porewater to saturation concentration. The latter can be expressed: $k_d \cdot (SDB_{sat} - SDB)$, where the kinetic rate k_d is a function of the temperature. The rate of dissolution is generally around $1.5.10^{-3} - 3.8.10^{-3}$ h^{-1} (House *et al.*, 2000).

Table 1 : Parameters definition

| Reaction	Equation	Parameter	Definition	Value	Reference
Degradation of organic carbon	$-k_{ib}*Corg_i$	k1b	First order degradation constant of organic carbon from the most degradable class (class I) at 20°C	$3.6.10^{-4}$-$5.4.10^{-4}h^{-1}$ 8.10^{-3} h^{-1}	Billen *et al.*, 1989 Sanchez, 1997
		k2b	First order degradation constant of organic carbon from class II (less degradable than class I) at 20°C	$2.1.10^{-5}$ h^{-1} 0.0005 h^{-1}	Billen *et al.*, 1989 Sanchez, 1997
		α	Stoechiometric coefficient relating oxygen consumption to organic carbon degradation	2.9 $gO2.gC^{-1}$	Billen *et al.*, 1989
		ε	Nitrogen fraction in the organic matter	0.17 $gN.gC^{-1}$	Redfield *et al.*, 1963
Denitrification	$(\lambda*\Sigma(Corg_i*k_{ib}))/$ $(2*Km_{NO3})$	Km_{NO3}	Michaelis constant for denitrification	25-50 $\mu moles.L^{-1}$	Billen *et al.*, 1989
		λ	Stoechiometric coefficient relating nitrate reduction to organic carbon degradation	66 $mmolesNO3.gC^{-1}$	Billen *et al.*, 1989
Primary production	$\delta*IPP$ $*exp(-\delta*z)$	IPP	Benthic primary production	0-30 $\mu gC.cm^{-2}.h^{-1}$	de Becker, 1986, Flipo *et al.* submitted
		δ	Depth attenuation factor	20 cm^{-1}	Flipo *et al.* submitted
Nitrification	$-(k_{ni}/(1+K))*NH_4$	kni	First order nitrification constant	$0.3 - 2.1$ h^{-1}	Henriksen and Kemp, 1988; Cébron, 2004
		K	First order adsorption constant for ammonium	$3 - 6$	Lerman, 1978, Billen *et al.*, 1989
Silica dissolution	$kd*(SDBsat-$ $SDB)$	kd	First order dissolution constant of silica	$1.5.10^{-3}$–$3.8.10^{-3}$ h^{-1}	House *et al.*, 2000
		SDBsat	Silica concentration in the porewater at saturation	12 $mgSiO2.L^{-1}$	Lerman, 1978
		UptSi	Stoechiometric coefficient relating silica consumption to primary production	0.33 $gSi.gC^{-1}$	Redfield *et al.*, 1963
Adsorption/ desorption of Phosphate		K_{PO4}	First order adsorption constant for phosphate	200	Garban *et al.*, 1995
		β	Phosphorus fraction in the organic matter	0.024 $gP.gC^{-1}$	Redfield *et al.*, 1963

Case studies

The purpose of this section is to test our benthic sub-model, independently of the 'main' water column model to which it is intended to be appended. We apply it here to some well-documented situations, representative of the range of conditions, which could be encountered within a river continuum. The case studies refer (i) to a storage reservoir on a 6th order river where high sedimentation conditions prevail, (ii) to a 8th order river with slow moving waters, and (iii) to a low order stream with fast flowing waters. For all three situations, direct empirical data are available to document both the fluxes at the sediment water interface, measured with benthic bell-jars, and the distribution of dissolved species in the sediment pore water, measured either on cores or with in-situ micro-electrodes.

The storage reservoir of Mery s/Oise

The raw water storage reservoir of Mery s/Oise has a capacity of 400 000 m^3 and a mean depth of 9 m. It is fed by the Oise River and is used for drinking water production. The main purpose of this basin is to carry on production in case of a pollution affecting the river. The storage basin is characterised by high sedimentation rates, as the retention time of the water in the basin is about 4 days. Direct measurement of fluxes across the sediment – water interface using benthic bell–jars and determination of organic carbon and nitrogen forms in the sediment were performed over a four-years period Billen *et al*. (1989). Data collected in September 1982 were exploited in this study as they presented the most complete data set in terms of nutrient fluxes and concentration profiles in the sediment. The model is fed with the observed values of the temperature and the total organic matter concentration in the upper fluid layer of the sediments, estimated to extend down to 1 cm depth, on the basis of porosity measurements. The kinetic parameters used are in the range of values presented in Table 1. Benthic primary production is set to zero, as light does not penetrates down to the bottom in this situation. The only adjustable parameters are the apparent diffusion coefficient in the upper fluid layer, as well as the fraction of rapidly versus slowly biodegradable organic material in the upper layer.

The calculated profiles of pore water nutrient concentrations, as well as the fluxes across the sediment water interface are compared in Figure 2 and Table 2b respectively.
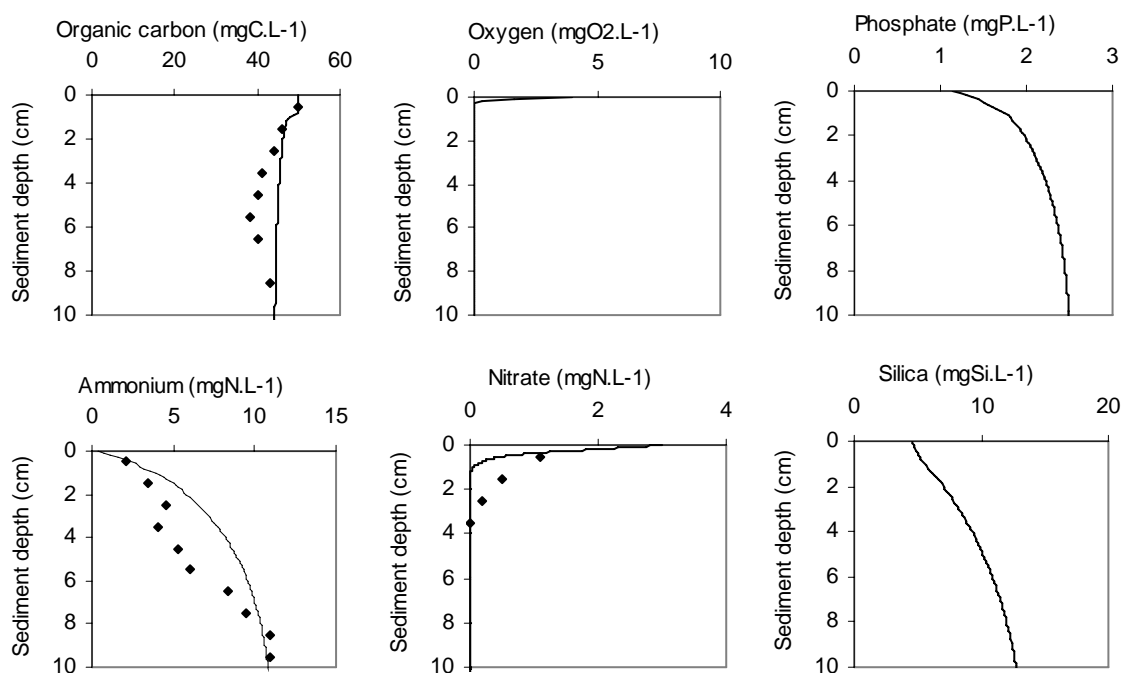
Figure 2: Organic carbon, oxygen, dissolved silica, ammonium, nitrate and phosphorus modelled and observed concentration profiles in the sediment of the Mery S/Oise storage reservoir in September 1982.

Table 2: a. Adjusted values of the apparent diffusion coefficient and biodegradability of organic material in the upper fluid layer of the sediment for simulating the condition in the the Mery S/Oise storage reservoir in September 1982.

Parameter	Value
D_f $(cm^2.h^{-1})$	0.09
$C_{org\ 1}$ (%)	6
$C_{org\ 2}$ (%)	6
$C_{org\ 3}$ (%)	88

b. Calculated and observed diffusive flux for nutrients and oxygen of the Mery S/Oise storage reservoir in September 1982. (Positive fluxes are directed from the water column to the sediment, while negative fluxes are directed to the water column)

Flux $(mg.m^{-2}.h^{-1})$	Observed	Modelled
O_2	22	26
NO_3	4	4
NH_4	-3	-3
PO_4		-0.8
SiO_2		-1

By adjusting the diffusion coefficient and the organic matter biodegradability in the upper fluid layer (Table 2a), the benthic sub-model, applied to the situation of the storage basin of Mery s/Oise, can provide results in good agreement with observed organic carbon, ammonium and nitrate concentrations profiles in the sediment. Oxygen is depleted within 1 cm depth of the sediment showing a high heterotrophic activity. The anaerobic conditions that prevail below this depth allow nitrate to be rapidly denitrified by bacteria. The result is a net consumption of oxygen and nitrate from the water column to oxidise the organic matter present in the sediment, the modelled fluxes being in very good agreement with the observed ones. Ammonium is produced by ammonification of the organic matter and only a small fraction is nitrified in the upper aerobic layer, so that a large flux of ammonium is diffusing to the water column, as indeed observed in the bell jars measurements.

The lower Seine River

The river Seine downstream of Paris at Porcheville is a regulated 8th order river draining an upstream basin of 61 800 km^2. The mean discharge of the Seine river at Paris is 210 m^3.s^{-1} (median value over the period 1974-2004) and ranges from 30 m^3.s^{-1} under drought conditions to 1790 m^3.s^{-1} during flood events. The Seine water depth is regulated and maintained at about 5 m. The wastewater purification plant of Achères, 25 km downstream from Paris, treats the wastewater of the 10 millions inhabitants of the Paris region, which represents about 30 m^3.s^{-1}, i.e. a discharge equal to the discharge of the Seine under dry conditions. Porcheville is located 35 km downstream of Achères.

The regulated river, under dry conditions, has depositional sedimentation characteristics similar to those of lakes, except that navigation creates a certain periodic turbulence Martin (2001). Data from Chesterikoff *et al.* (1992) and Garban *et al.* (1995) where exploited for the validation of the benthic sub-model. They comprise measurements of nutrients and oxygen flux at the sediment-water interface by means of benthic bell-jars in June 1990 and May 1991, as well as nutrients concentrations profiles in the sediments obtained by dialysis cells in May 1992. During low flow periods, apparent sedimentation rates of suspended matter, estimated with sediment traps, were around 3.5g.m^{-2}.h^{-1} at Porcheville (March 1992). Using these data we set the model to represent the concentration profiles of nutrients in the sediment over May 1992. Again the only parameters not set by direct independent evaluations are the diffusion coefficient of the upper fluid layer and the biodegradability of the organic matter.

The results obtained are compared with measurements in Fig 3 and Table 3.
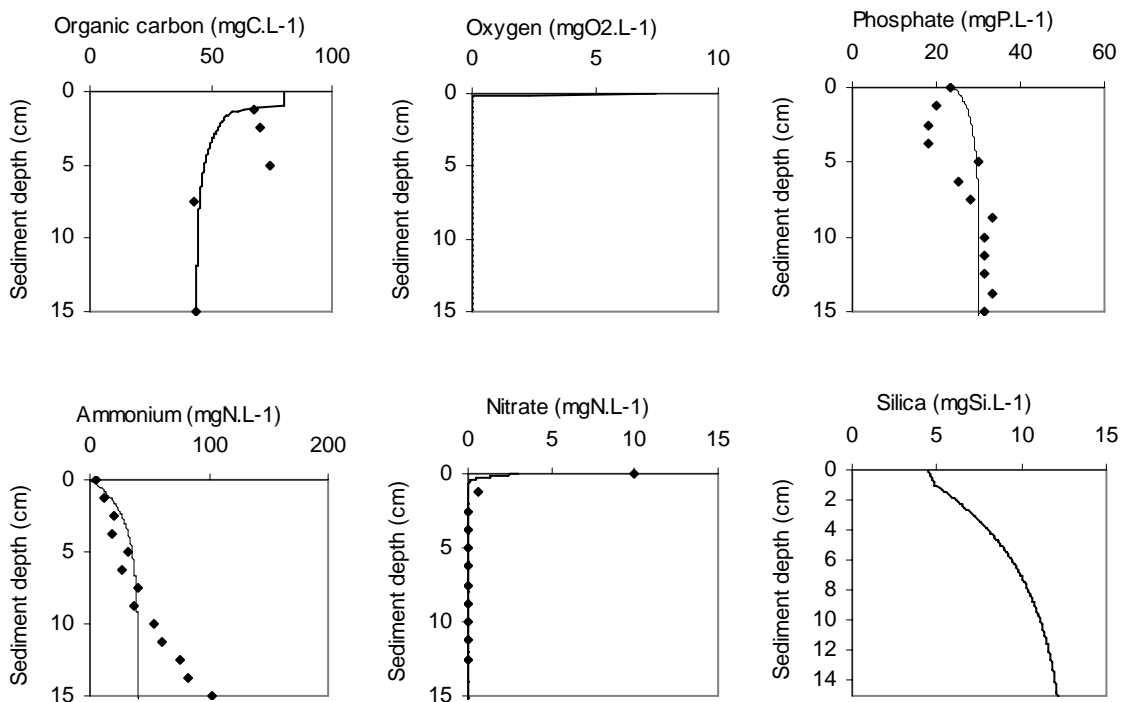
Figure 3: Organic carbon, oxygen, dissolved silica, ammonium, nitrate and phosphorus modelled and observed concentration profiles in the sediment of the Seine river at the Porcheville station in May 1992.

Table 3:

a. Adjusted values of the apparent diffusion coefficient and biodegradability of organic material in the upper fluid layer of the sediment for simulating the condition of the river Seine at Porcheville in May 1992.

Parameter	Value
D_f ($cm^2.h^{-1}$)	0.18
$C_{org\ 1}$ (%)	25
$C_{org\ 2}$ (%)	20
$C_{org\ 3}$ (%)	55

b. Calculated and observed diffusive flux for nutrients and oxygen in the river Seine at Porcheville in May 1992. (Positive fluxes are directed from the water column to the sediment, while negative fluxes are directed to the water column)

Flux ($mg.m^{-2}.h^{-1}$)	Observed	Modelled
O_2	70 / 170	121
NO_3	12 / 13	14
NH_4	-28 / -36	-36
PO_4	-8 / -8.5	-7
SiO_2		-0.7

Again, for suitable values of the two adjustable parameters, the application of the benthic sub-model provides results in good agreement with the available observations, including for phosphate flux and pore water distribution, which were not available for the Méry data set. The simulation of ammonium distribution, however, does not fit the data below 10 cm depth in the sediments. This probably results from the fact that our model does only take into account the most biodegradable fractions of organic matter and considers the remaining material as absolutely refractory, while, in reality, this material undergoes a slow degradation, which might explain the further increase of pore water ammonium concentration in the deeper layers of the sediment.

Compared with the Méry situation, both the model and the observations show higher fluxes of oxygen and nutriments in the Seine River. This is explained by a higher sedimentation rate and organic content of the depositing material, due to the proximity of the wastewater treatment plant of Achères.

The Orneau headwater stream

The Orneau river at La Sauvenière, near Gembloux is a 2nd order stream of the Meuse drainage network, originating in the loess plateau of central Belgium. Data from de Becker (1986) are exploited in this case study to test the applicability of the model to a small stream. The data available are the organic carbon content of the upper sediment layer and the oxygen, ammonium and nitrate flux measured with a benthic bell-jar experiment in May 1982. Unfortunately, no pore water chemistry measurements are available for this situation. This situation also differs from the previous ones by the fact that light penetrates down to the bottom in this shallow stream, so that benthic primary production can occur on the top layer of the sediments. This is an additional forcing variable that we have to adjust, within the range of observed values in small streams (0 to 120 mgC/m²/h, de Becker, 1986). The results obtained with the model, when adjusting the unknown forcing parameters and variables, are compared with the data in Figure 4 and Table 4.
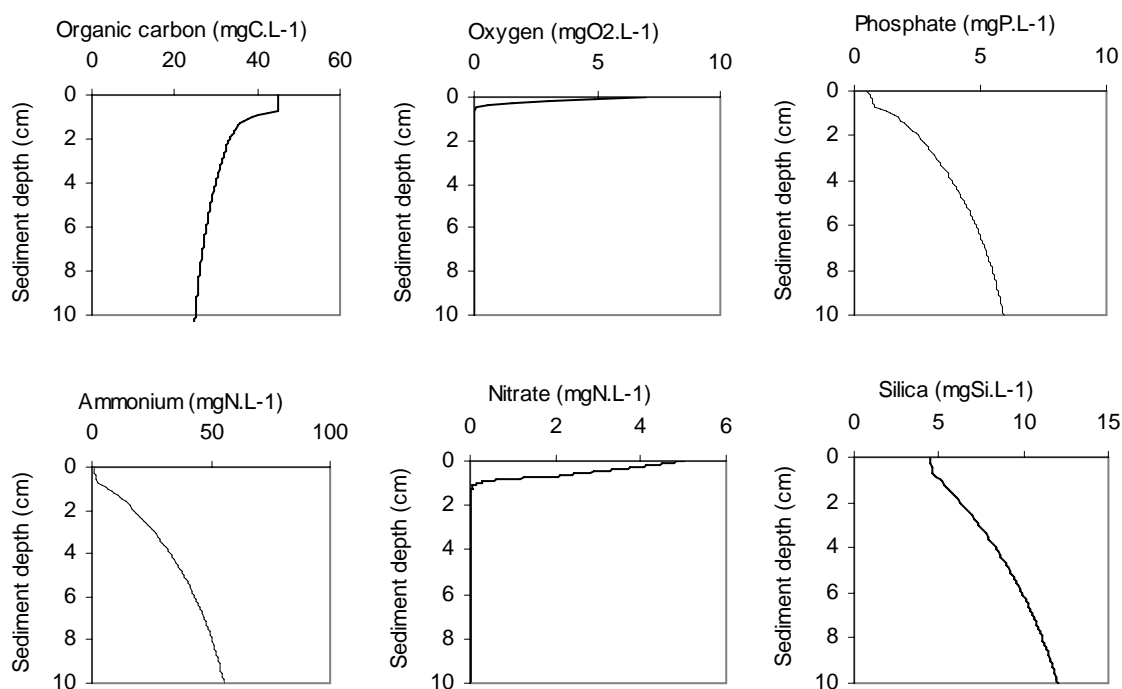
Figure 4: Organic carbon, oxygen, dissolved silica, ammonium, nitrate and phosphorus modelled concentration profiles in the sediment of the Orneau stream in May 1983 using the bi-layer model.

Table 4:

a. Values of the parameters used for simulating the situation of the Orneau stream.

Parameter	Value
D_f (cm^2.h^{-1})	0.35
$C_{org\ 1}$ (%)	20
$C_{org\ 2}$ (%)	30
$C_{org\ 3}$ (%)	50

b. Calculated and observed diffusive flux for nutrients and oxygen of the Orneau stream in May 1983.

Flux (mg.m^{-2}.h^{-1})	Observed	Modelled
O_2	70	70
NO_3	14	13
NH_4	-5	-5
PO_4		-2
SiO_2		1

Here again, the model is able to correctly reproduce the observed fluxes of oxygen, nitrate and ammonium across the sediment-water interface (Table 4). Compared to the two previous case studies, it appears that nutrients and oxygen fluxes across the interface are surprisingly high for such a small stream, with relatively low sedimentation. In this case, inputs of a highly biodegradable organic matter, originating both from deposition of vegetal fragments and from in situ primary production, are responsible for the high benthic biogeochemical activity.

The dissolved silica variable could not be fully tested as no data where available in the case studies chosen. However, the model could be validated for organic carbon, ammonium, nitrate and phosphorus in terms of profiles in the sediment and for oxygen, ammonium, phosphorus and nitrate in terms of flux across the interface.

Sensitivity to physical and biogeochemical driving factors

In all three above case studies, the model is able to reproduce the observed fluxes of oxygen, dissolved nitrogen and phosphate across the sediment water interface, as well as the vertical distribution of dissolved and particulate forms of these nutrients within the sediment. The situations studied differ in term of physical factors (determining the mixing of the upper sediment layer) and biogeochemical factors (including the amount and quality of organic material brought to the upper layer of the sediment, either by sedimentation of by in-situ benthic primary production).

A sensitivity analysis is performed here to understand how the modelled oxygen and nutrients fluxes are affected by these two classes of driving factors. The Orneau case study was chosen for this analysis as it represents a low order stream where the monolayer model could also be applied if the erosion process was higher than the deposition process. The reference situation used to run the sensitivity tests thus corresponds to the results presented in Figure 4 and Table 4. The same parameter values were also used for the monolayer model.

Physical driving factors
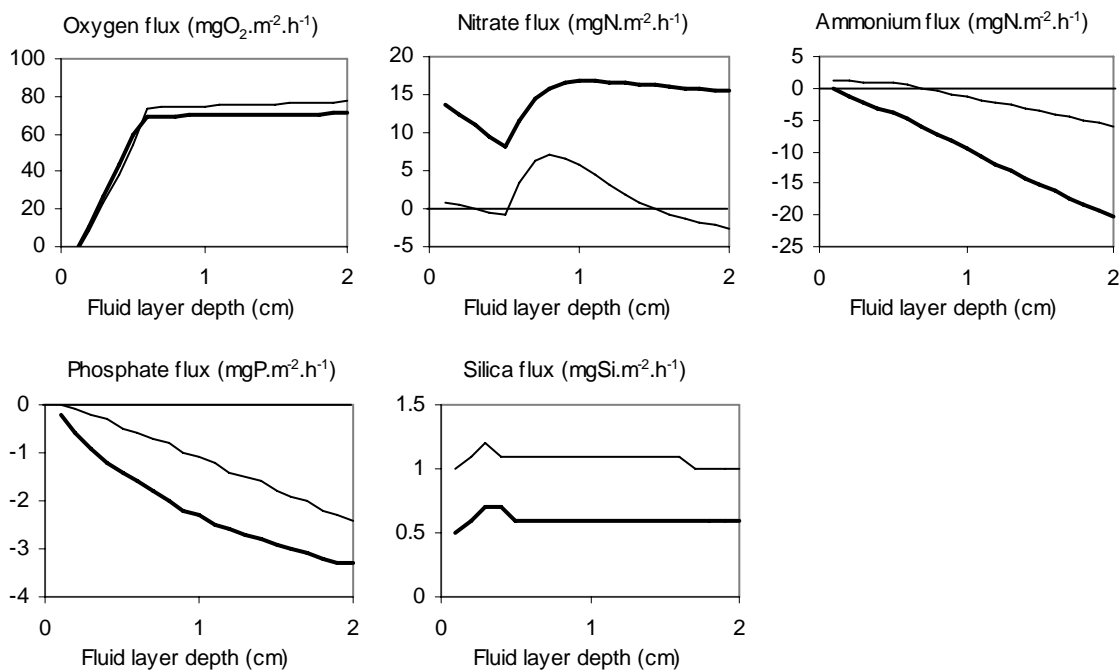
Figure 5: Oxygen, nitrate, ammonium, inorganic dissolved phosphorus and dissolved silica fluxes modelled for varying depth of the fluid layer, using the bi-layer model (bold curve) or the single layer model (thin curve), for the conditions of the Orneau stream in May 1983. (Positive fluxes are directed from the water column to the sediment, while negative fluxes are directed to the water column)

Firstly, we tested the influence of the depth of the fluid layer over the oxygen and nutrients fluxes across the sediment-water interface using both models (bi-layer and monolayer models (Figure 5)). The oxygen and silica fluxes increase up to a plateau, reached when the fluid layer is about 0.7 cm in both model applications. The oxygen flux increases with the depth of the fluid layer until the latter becomes deeper than the aerobic layer: from this point on, the degradation of organic carbon, the concentration of which is set constant throughout the fluid layer in the model, produces exactly the same gradient of oxygen at the water sediment

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interface, hence the same flux, whatever the depth of the fluid layer. For the silica flux, linked to the uptake by active benthic diatoms, the predicted response to increased depth of the fluid layer results from the fact that the model considers a distribution of primary production restricted to the very top layer of the sediment. Once the fluid layer is deep enough to contain the active primary production layer, the effect of this process remains the same.

For nitrate, at very low depth of the fluid layer, the flux decreases first with deeper fluid layer, because more nitrification can occur. Once the point is reached that the oxic layer is shallower than the fluid layer, denitrification can take place in the fluid layer, thus increasing the nitrate demand. A plateau is reached when nitrate reaches depletion within the fluid layer. Note that the response of the monolayer model differs from that of the bi-layer model, because no denitrification can occur below the fluid layer, thus favouring the effect of nitrification. Interestingly, the net nitrate consumption is maximum for a depth of the biofilm between 0.5 and 1.5 cm.

For ammonium, the flux released across the sediment water interface increases with the depth of the fluid layer, more rapidly when the latter is entirely oxic, more slowly when $zn<zf$. Here again, the response of the mono-layer model differs, predicting a net flux of ammonium consumption from the water column (net nitrification) as long as the biofilm is entirely oxic.

The phosphate flux responds in the same way as ammonium for both models, except that our model does not differentiate between oxic and anoxic behaviour for phosphate adsorption processes. A regular increase of phosphorus release is therefore observed with increasing depth of the fluid layer.
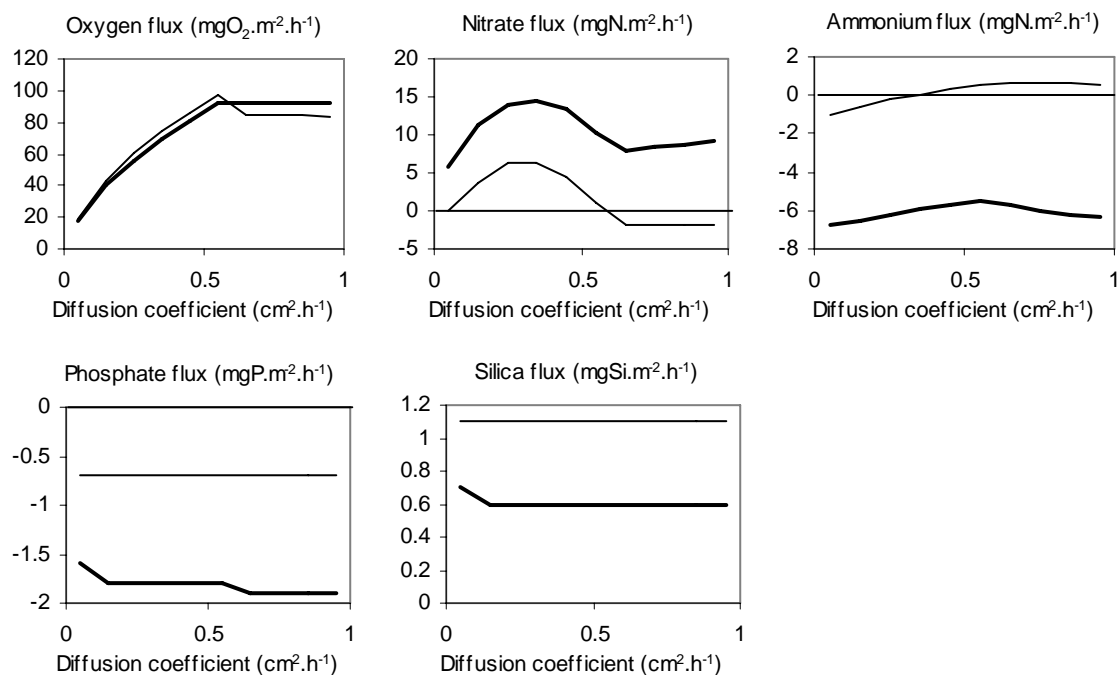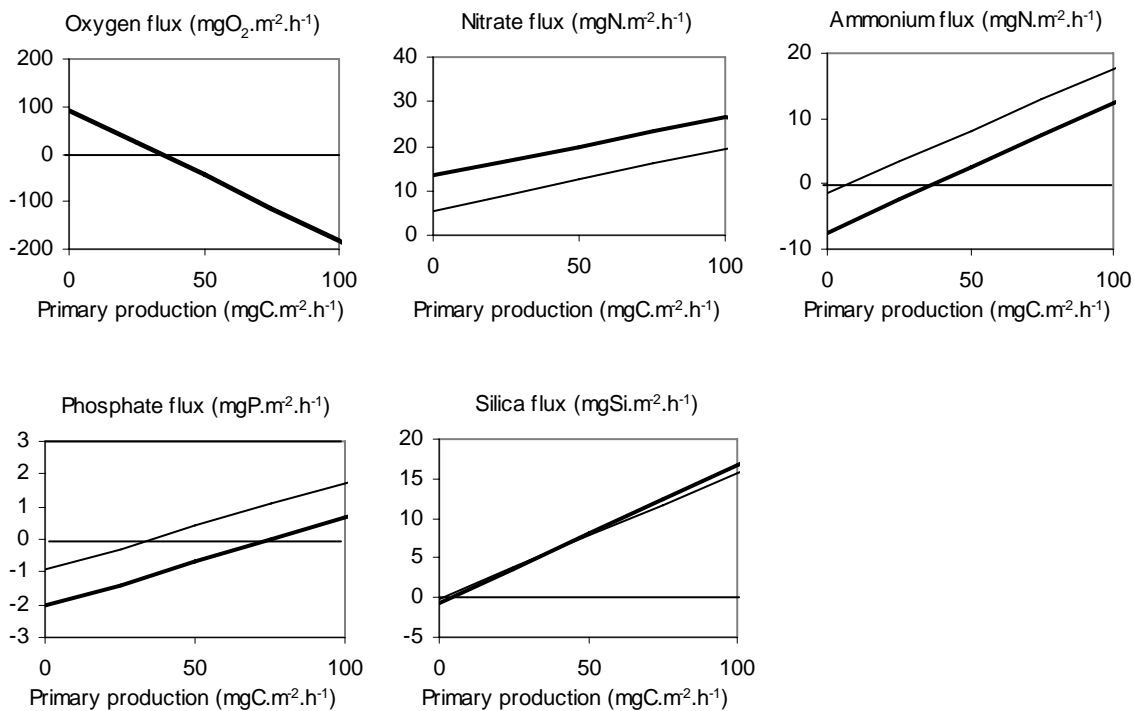

Figure 6: Oxygen, nitrate, ammonium, inorganic dissolved phosphorus and dissolved silica fluxes modelled for various diffusion coefficient in the fluid layer using the bi-layer model (-) or the single layer model (-) over the Orneau stream in May 1983. (Positive fluxes are directed from the water column to the sediment, while negative fluxes are directed to the water column)

Figure 6 shows the effect of varying the diffusion coefficient in the upper fluid layer set at a depth of 0.7 cm. The silica flux is largely independent on diffusion, as it is mostly determined by the uptake by benthic diatoms. Note that the monolayer model, which cannot represent any storage of biogenic silica (contrarily to the bi-layer model which accumulates material within the compacting deeper layer) predicts a lower net uptake. The same applies to phosphate that depends on the equilibrium between dissolved and particulate inorganic phosphorus.

The response of the oxygen flux is an increase with increasing diffusion up to the point where the fluid layer is entirely oxic. For the same reason, nitrate flux first increases then decrease again because the local rate of denitrification in the sediment decreases when the oxic layer penetrates deeper into the compacted layer. With the monolayer model, the biofilm is predicted to be a net consumer of nitrate only below a diffusion coefficient of $0.5 \text{ cm}^2.\text{h}^{-1}$.

For ammonium, the increase of the aerobic layer with increasing diffusion increases the nitrification process, thus reducing the flux of ammonium released across the sediment water interface, up to the point where the fluid layer is entirely oxic.

Biogeochemical driving factors

Figure 7: Oxygen, nitrate, ammonium, inorganic dissolved phosphorus and dissolved silica fluxes modelled for various primary production in the fluid layer using the bi-layer model (-) or the single layer model (-) over the Orneau stream in May 1983. (Positive fluxes are directed from the water column to the sediment, while negative fluxes are directed to the water column)

Figure 7 presents the response of the model to varying intensity of benthic primary production from 0 to 100 $\text{mgC.m}^{-2}.\text{h}^{-1}$ (Flipo *et al.*, submitted; de Becker, 1986). Obviously, an increase in primary production results in higher oxygen production and higher ammonium, phosphate and silica consumption, thus affecting the resulting fluxes accordingly.
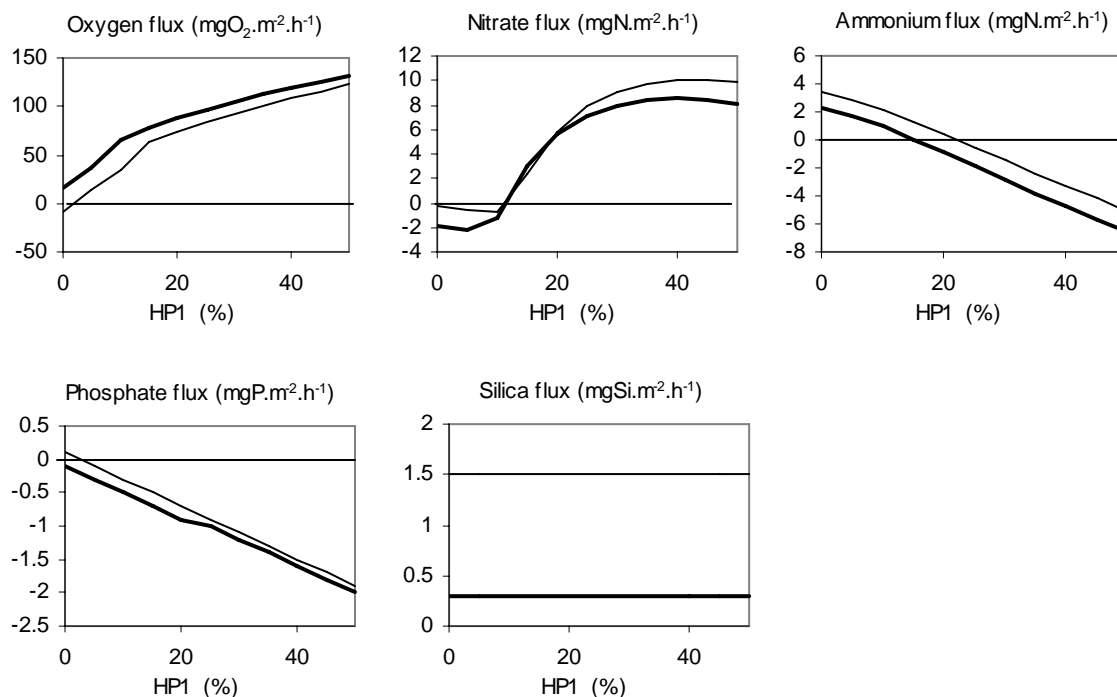
Figure 8: Oxygen, nitrate, ammonium, inorganic dissolved phosphorus and dissolved silica fluxes modelled for various percentage of each class of biodegradable organic carbon using the bi-layer model (-) or the single layer model (-) over the Orneau stream in May 1983. (Positive fluxes are directed from the water column to the sediment, while negative fluxes are directed to the water column)

Figure 8 shows the response of the model to increased biodegradability of the organic material present in the fluid layer. For this exercise, the total biodegradable organic matter content is kept constant, while the fraction of rapidly biodegradable carbon ($Corg_1$) is varied from 0 (all biodegradable carbon is $Corg_2$) to 50% (all is $Corg_1$).

The effect is significant for oxygen, ammonium, nitrate and phosphate flux but not for silica flux as could be expected. The more class I biodegradable carbon, the faster the rate of organic matter degradation, the higher oxygen and nutrients fluxes across the interface. For nitrate, under low organic matter biodegradability, the production of nitrate through nitrification dominates over denitrification while the reverse is true at high biodegradability. For ammonium and phosphate, in the case of the monolayer model, if the organic carbon biodegradability is low then the release of these nutrients through organic matter degradation can be lower than their uptake by primary production.

The sensitivity analysis presented here illustrates the complexity of the interacting reactions driving each variable. In this context, the usefulness of the model is clear in order to understand and predict the behaviour of this complex system.

Conclusion

In this paper, we have described a generic benthic sub-model that represents early-diagenetic processes in the superficial sediments of freshwater ecosystems. The basic hypothesis is that the same processes are operative throughout the river continuum (same kinetics parameters). Only the constraints that can be calculated by the main hydrological model vary over the river continuum like concentration of nutrients and oxygen in the overlying water, primary production and the concentration of organic carbon in the superficial layer of sediment. The model incorporates a number of simplifying assumptions in order to allow its integration into the 'main' river continuum hydrological-biogeochemical model. Thus steady state diagenesis is assumed in the benthic model; constant concentrations of particulate matter in the upper fluid layer, as well as constant porosity over each layer. In spite of these simplifying and debatable assumptions, the model is able to successfully represent ammonium, nitrate, oxygen and phosphorus fluxes at the sediment water interface. Moreover, the model is applicable to a wide range of sedimentation conditions and sediment organic content and can represents the interdependent behaviour of a large number of variables (organic carbon, oxygen, phosphorus, silica, ammonium and nitrate). Therefore, it answers the objective of providing a generic benthic sub-model that could be linked to any hydrological / water quality model to examine the effects of benthic processes on the water column composition, particularly in terms nitrogen, phosphorus and silica, the main nutrients responsible for the eutrophication of water bodies.

Acknowledgements

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Appendix 1: Analytical solutions of the diagenetic equations

1. Bi-layer model

The model describes the distribution of all variables within an upper fluid layer of fixed depth, overlying a compacted infinite sediment layer. Organic carbon ($Corg_{1f}$, $Corg_{2f}$, $Corg_{3f}$), biogenic silica (BBS_f) and total inorganic phosphorus (PIT_f) are considered constant over the fluid layer at a value given by the main model. The indices f and relates to the layer of sediment fluid or compacted.

1.1 Particulate variables

1.1.1 Organic carbon

The benthic sub-model calculates the concentrations of particulate matters in the compacted layer. The diagenetic equation of organic carbon in the compacted layer can be written as:

$$\frac{\partial Corg(i)}{\partial t} = -w \cdot \frac{\partial Corg(i)}{\partial z} - k1b \cdot Corg(i) \tag{1}$$

The solution of equation (1) can be expressed as:

$$Corg_{ic} = \frac{1-\phi_c}{1-\phi_f} \cdot Corg_{if} \cdot e^{-\frac{kib}{w} \cdot \left(z - z_f\right)}$$

1.1.2 Biogenic silica

The diagenetic equation of biogenic silica in the compacted layer can be written as:

$$\frac{\partial BBS}{\partial t} = -w \cdot \frac{\partial BBS}{\partial z} - kd \cdot \left(SDB_{sat} - SDB\right) \tag{2}$$

The solution of equation (2) is:

$$BBS_c = \frac{kd}{w} \cdot \left(\frac{A_{37} \cdot e^{a_{37} \cdot z}}{a_{37}}\right) + F_{41}$$, with A_{37} as determined in the resolution of the dissolved silica

diagenetic equation.

With the boundary conditions:

$$z = z_f : \frac{BBS_c}{\left(1-\phi_c\right)} = \frac{BBS_f}{\left(1-\phi_f\right)}$$

Then, $F_{41} = BBS_f \cdot \frac{\left(1-\phi_c\right)}{\left(1-\phi_f\right)} - \frac{kd}{w} \cdot \left(\frac{A_{37}}{a_{37}} \cdot e^{a_{37} \cdot z_f}\right)$

1.2 Dissolved variables

1.2.1 Ammonium

Oxygen conditions affect the processes that are included in the ammonium diagenetic equation. In return, nitrification uses oxygen and needs to be determined first.

zn<zf: For ammonium, if the aerobic layer is shallower than the fluid layer (zn<zf), the diagenetic equations for ammonium can be written as:

Fluid & aerobic layer:

$$\frac{\partial NH_4}{\partial t} = D_f \frac{\partial^2 NH_4}{\partial z^2} - w \cdot (1+K) \cdot \frac{\partial NH_4}{\partial z} - kni \cdot NH_4 + \varepsilon \cdot \left(k1b \cdot Corg1_f + k2b \cdot Corg2_f \right) - uptNH_4 \cdot e^{-\delta \cdot z} \tag{3}$$

Fluid & anaerobic layer:

$$\frac{\partial NH_4}{\partial t} = D_f \frac{\partial^2 NH_4}{\partial z^2} - w \cdot (1+K) \cdot \frac{\partial NH_4}{\partial z} + \varepsilon \cdot \left(k1b \cdot Corg1_f + k2b \cdot Corg2_f \right) - uptNH_4 \cdot e^{-\delta \cdot z} \tag{4}$$

Compacted & anaerobic layer:

$$\frac{\partial NH_4}{\partial t} = D_c \frac{\partial^2 NH_4}{\partial z^2} - w \cdot (1+K) \cdot \frac{\partial NH_4}{\partial z} + \varepsilon \cdot \frac{1-\phi_c}{1-\phi_f} \cdot \left(Corg1_f \cdot k1b \cdot e^{-\frac{k1b}{w}\left(z-z_f\right)} + Corg2_f \cdot k2b \cdot e^{-\frac{k2b}{w}\left(z-z_f\right)} \right) \tag{5}$$

The solution of equations (3), (4) and (5) can be written as:

(3): $\left(NH_4 \right)_n = A_5 \cdot e^{a_5 \cdot z} + A_6 \cdot e^{a_6 \cdot z} + F_4 \cdot e^{-\delta \cdot z} + F_5$ with, $w' = w(1+K)$, $a_5 = \frac{w' - \sqrt{w'^2 + 4 \cdot D_f \cdot kni}}{2 \cdot D_f}$,

$a_6 = \frac{w' + \sqrt{w'^2 + 4 \cdot D_f \cdot kni}}{2 \cdot D_f}$, $F_4 = \frac{uptNH_4}{D_f \cdot \delta^2 + w' \cdot \delta - kni}$ and $F_5 = \frac{\varepsilon \cdot r}{kni}$; avec $r = \left(k1b \cdot Corg_{1f} + k2b \cdot Corg_{2f} \right)$

(4): $\left(NH_4 \right)_f = A_7 + A_8 \cdot e^{a_8 \cdot z} + F_6 \cdot e^{-\delta \cdot z} + F_7 \cdot z$,   with $a_8 = \frac{w'}{D_f}$, $F_6 = \frac{uptNH_4}{D_f \cdot \delta^2 + w' \cdot \delta}$ and $F_7 = \frac{\varepsilon \cdot r}{w'}$

(5): $\left(NH_4 \right)_c = A_9 + F_8 \cdot e^{-\frac{k1b}{w}\left(z-z_f\right)} + F_9 \cdot e^{-\frac{k2b}{w}\left(z-z_f\right)}$,   with $F_8 = \dfrac{-\varepsilon \cdot k1b \cdot \left(\dfrac{1-\phi_c}{1-\phi_f}\right) \cdot Corg1_f}{D_f \cdot \left(\dfrac{k1b}{w}\right)^2 + (1+K) \cdot k1b}$

and $F_9 = \dfrac{-\varepsilon \cdot k2b \cdot \left(\dfrac{1-\phi_c}{1-\phi_f}\right) \cdot Corg2_f}{D_f \cdot \left(\dfrac{k2b}{w}\right)^2 + (1+K) \cdot k2b}$

With the boundary conditions:

$z = 0$, $\left(NH_4 \right)_n = NH_{40}$, ammonium concentration in the water column

$z = zf$, $\dfrac{NH_{4f}}{\phi_f} = \dfrac{NH_{4c}}{\phi_c}$; $z=zf$, $D_f \cdot \left(\dfrac{\partial NH_4}{\partial z} \right)_f = D_c \cdot \left(\dfrac{\partial NH_4}{\partial z} \right)_c$;

$z=zn$, $\left(\dfrac{\partial NH_4}{\partial z} \right)_n = \left(\dfrac{\partial NH_4}{\partial z} \right)_f$ and $z=zn$, $\left(NH_4 \right)_n = \left(NH_4 \right)_f$

Thus,

$A_5 = NH_{40} - A_6 - F_4 - F_5$

$$A_8 = \frac{\dfrac{D_c}{D_f}\left(-\dfrac{k1b}{w} \cdot F_8 - \dfrac{k2b}{w} \cdot F_9 \right) - F_7 + \delta \cdot F_6 \cdot e^{-\delta \cdot z_f}}{a_8 \cdot e^{a_8 \cdot z_f}}$$

$$A_9 = \frac{\phi_c}{\phi_f}\left(A_7 + A_8 \cdot e^{a_8 \cdot z_f} + F_6 \cdot e^{-\delta \cdot z_f} + F_7 \cdot z_f \right) - F_8 - F_9$$

$$A_6 = \frac{\left(a_8 \cdot A_8 \cdot e^{a_8 \cdot z_n} - \delta \cdot (F_6 - F_4) \cdot e^{-\delta \cdot z_n} + F_7 - a_5 \cdot (NH_{40} - F_4 - F_5) \cdot e^{a_5 \cdot z_n}\right)}{a_6 \cdot e^{a_6 \cdot z_n} - a_5 \cdot e^{a_5 \cdot z_n}}$$

$$A_7 = e^{a_5 \cdot z_n} \cdot (NH_{40} - F_4 - F_5) + A_6 \cdot \left(e^{a_6 \cdot z_n} - e^{a_5 \cdot z_n}\right) + (F_4 - F_6) \cdot e^{-\delta \cdot z_n} - F_7 \cdot z_n + F_5 - A_8 \cdot e^{a_8 \cdot z_n}$$

zn>zf: For ammonium, if the aerobic layer is deeper than the fluid layer (zn>zf), the diagenetic equations for ammonium can be written as:

Fluid & aerobic layer:

$$\frac{\partial NH_4}{\partial t} = D_f \frac{\partial^2 NH_4}{\partial z^2} - w \cdot (1+K) \cdot \frac{\partial NH_4}{\partial z} - kni \cdot NH_4 + \varepsilon \cdot \left(k1b \cdot Corg1_f + k2b \cdot Corg2_f\right) - uptNH_4 \cdot e^{-\delta \cdot z} \tag{6}$$

Compacted & aerobic layer:

$$\frac{\partial NH_4}{\partial t} = D_c \frac{\partial^2 NH_4}{\partial z^2} - w \cdot (1+K) \cdot \frac{\partial NH_4}{\partial z} - kni \cdot NH_4 + \varepsilon \cdot \left(k1b \cdot Corg1_f + k2b \cdot Corg2_f\right) \tag{7}$$

Compacted & anaerobic layer:

$$\frac{\partial NH_4}{\partial t} = D_c \frac{\partial^2 NH_4}{\partial z^2} - w \cdot (1+K) \cdot \frac{\partial NH_4}{\partial z} + \varepsilon \cdot \frac{1-\phi_c}{1-\phi_f} \cdot \left(Corg1_f \cdot k1b \cdot e^{-\frac{k1b}{w}(z - z_f)} + Corg2_f \cdot k2b \cdot e^{-\frac{k2b}{w}(z - z_f)}\right) \tag{8}$$

The solution of equations (6), (7) and (8) can be written as:

(6): $(NH_4)_f = A_{13} \cdot e^{a_{13} \cdot z} + A_{14} \cdot e^{a_{14} \cdot z} + F_{10} \cdot e^{-\delta \cdot z} + F_{11}$, with $a_{13} = \dfrac{w' - \sqrt{w'^2 + 4 \cdot D_f \cdot kni}}{2 \cdot D_f}$,

$a_{14} = \dfrac{w' + \sqrt{w'^2 + 4 \cdot D_f \cdot kni}}{2 \cdot D_f}$, $F_{10} = \dfrac{uptNH_4}{D_f \cdot \delta^2 + w' \cdot \delta - kni}$ and $F_{11} = \dfrac{\varepsilon \cdot r}{kni}$

(7): $(NH_4)_n = A_{15} \cdot e^{a_{15} \cdot z} + A_{16} \cdot e^{a_{16} \cdot z} + F_{12} \cdot e^{-\frac{k1b}{w}\cdot(z - z_f)} + F_{13} \cdot e^{-\frac{k2b}{w}\cdot(z - z_f)}$ with, w'=w(1+K),

$a_{15} = \dfrac{w' - \sqrt{w'^2 + 4 \cdot D_c \cdot kni}}{2 \cdot D_c}$, $a_{16} = \dfrac{w' + \sqrt{w'^2 + 4 \cdot D_c \cdot kni}}{2 \cdot D_c}$, $F_{12} = \dfrac{-\varepsilon \cdot \dfrac{1-\phi_c}{1-\phi_f} \cdot Corg1_f \cdot k1b}{D_c \cdot \left(\dfrac{k1b}{w}\right)^2 + w' \cdot \left(\dfrac{k1b}{w}\right) - kni}$ and

$$F_{13} = \frac{-\varepsilon \cdot \dfrac{1-\phi_c}{1-\phi_f} \cdot Corg2_f \cdot k2b}{D_c \cdot \left(\dfrac{k2b}{w}\right)^2 + w' \cdot \left(\dfrac{k2b}{w}\right) - kni}$$

(8): $(NH_4)_c = A_{17} + F_{14} \cdot e^{-\frac{k1b}{w}\cdot(z - z_f)} + F_{15} \cdot e^{-\frac{k2b}{w}\cdot(z - z_f)}$, with $F_{14} = \dfrac{-\varepsilon \cdot k1b \cdot \left(\dfrac{1-\phi_c}{1-\phi_f}\right) \cdot Corg1_f}{D_c \cdot \left(\dfrac{k1b}{w}\right)^2 + (1+K) \cdot k1b}$

and $F_{15} = \dfrac{-\varepsilon \cdot k2b \cdot \left(\dfrac{1-\phi_c}{1-\phi_f}\right) \cdot Corg2_f}{D_c \cdot \left(\dfrac{k2b}{w}\right)^2 + (1+K) \cdot k2b}$

With the boundary conditions:

$z = 0$, $(NH_4)_f = NH_{40}$, ammonium concentration in the water column

$$z = zf, \quad \frac{NH_{4f}}{\phi_f} = \frac{NH_{4c}}{\phi_c} \; ; \qquad z = zf, \quad D_f \cdot \left(\frac{\partial NH_4}{\partial z}\right)_f = D_c \cdot \left(\frac{\partial NH_4}{\partial z}\right)_c \; ;$$

$$z = zn, \quad \left(\frac{\partial NH_4}{\partial z}\right)_n = \left(\frac{\partial NH_4}{\partial z}\right)_c \quad \text{and} \quad z = zn, \quad (NH_4)_n = (NH_4)_f$$

Thus,

$$A_{13} = NH_{40} - A_{14} - F_{10} - F_{11}$$

$$A_{15} = \frac{\frac{k1b}{w} \cdot (F_{12} - F_{14}) \cdot e^{-\frac{k1b}{w} \cdot (z_n - z_f)} + \frac{k2b}{w} \cdot (F_{13} - F_{15}) \cdot e^{-\frac{k2b}{w} \cdot (z_n - z_f)} - a_{16} \cdot A_{16} \cdot e^{a_{16} \cdot z_n}}{a_{15} \cdot e^{a_{15} \cdot z_n}}$$

$$A_{17} = A_{15} \cdot e^{a_{15} \cdot z_n} + A_{16} \cdot e^{a_{16} \cdot z_n} + (F_{12} - F_{14}) \cdot e^{-\frac{k1b}{w} \cdot (z_n - z_f)} + (F_{13} - F_{15}) \cdot e^{-\frac{k2b}{w} \cdot (z_n - z_f)}$$

$$A_{14} = \frac{\frac{D_c}{D_f}\left(a_{15} \cdot A_{15} \cdot e^{a_{15} \cdot z_f} + a_{16} \cdot A_{16} \cdot e^{a_{16} \cdot z_f} - \frac{k1b}{w} \cdot F_{12} - \frac{k2b}{w} \cdot F_{13}\right) - a_{13} \cdot e^{a_{13} \cdot z_f}(NH_{40} - F_{10} - F_{11}) + \delta \cdot F_{10} \cdot e^{-\delta \cdot z_f}}{a_{14} \cdot e^{a_{14} \cdot z_f} - a_{13} \cdot e^{a_{13} \cdot z_f}}$$

$$B = \delta \cdot F_{10} \cdot e^{-\delta \cdot z_f} - a_{13} \cdot e^{a_{13} \cdot z_f} \cdot (NH_{40} - F_{10} - F_{11})$$

$$C = -\frac{k1b}{w} \cdot F_{12} - \frac{k2b}{w} \cdot F_{13}$$

$$D = \frac{k1b}{w} \cdot (F_{12} - F_{14}) \cdot e^{-\left(\frac{k1b}{w}\right) \cdot (z_n - z_f)} + \frac{k2b}{w} \cdot (F_{13} - F_{15}) \cdot e^{-\left(\frac{k2b}{w}\right) \cdot (z_n - z_f)}$$

$$E = \frac{e^{a_{14} \cdot z_f} - e^{a_{13} \cdot z_f}}{a_{14} \cdot e^{a_{14} \cdot z_f} - a_{13} \cdot e^{a_{13} \cdot z_f}}$$

$$F = F_{10} \cdot e^{-\delta \cdot z_f} + e^{a_{13} \cdot z_f} \cdot (NH_{40} - F_{10} - F_{11}) + F_{11}$$

$$A_{16} = \frac{\frac{\phi_c}{\phi_f} \cdot F - F_{12} - F_{13} - \frac{D \cdot e^{a_{15} \cdot (z_n - z_f)}}{a_{15}} + \frac{\phi_c}{\phi_f} \cdot E \cdot \left(\frac{D_c}{D_f} \cdot \left(D \cdot e^{a_{15} \cdot (z_f - z_n)} + C\right) + B\right)}{e^{a_{16} \cdot z_f} - \frac{a_{16} \cdot e^{a_{16} \cdot z_n} \cdot e^{a_{15} \cdot z_f}}{a_{15} \cdot e^{a_{15} \cdot z_n}} + \frac{\phi_c \cdot D_c}{\phi_f \cdot D_f} \cdot E \cdot \left(a_{16} \cdot e^{a_{15} \cdot (z_f - z_n)} \cdot e^{a_{16} \cdot z_n} + a_{16} \cdot e^{a_{16} \cdot z_f}\right)}$$

1.2.2 Oxygen

zn<zf: For oxygen, the diagenetic equations if the aerobic layer is shallower than the fluid layer can be written as:

$$\frac{\partial O_2}{\partial t} = D_f \frac{\partial^2 O_2}{\partial z^2} - u \cdot \frac{\partial O_2}{\partial z} - \alpha \cdot \left(k1b \cdot Corg1_f + k2b \cdot Corg2_f\right) - \frac{4.5 \cdot kni}{(1+K)} \cdot NH_4(z) + \mathrm{Prod}O_2 \cdot e^{-\delta z} \qquad (9)$$

The solution of equation (9) can be written as:

$$O_2 = A_{19} \cdot e^{a_{19} \cdot z} + A_{20} + F_{16} \cdot e^{-\delta \cdot z} + F_{17} \cdot e^{a_6 \cdot z} + F_{18} \cdot e^{a_5 \cdot z} + F_{19} \cdot z, \qquad \text{with} \qquad a_{19} = \frac{u}{D_f},$$

$$F_{16} = \frac{\frac{4.5 \cdot kni \cdot F_4}{(1+K)} - \mathrm{Prod}O_2}{D_f \cdot \delta^2 + u \cdot \delta}, \quad F_{17} = \frac{\frac{4.5 \cdot kni \cdot A_6}{(1+K)}}{D_f \cdot a_6^2 - u \cdot a_6}, \quad F_{18} = \frac{\frac{4.5 \cdot kni \cdot A_5}{(1+K)}}{D_f \cdot a_5^2 - u \cdot a_5}, \quad F_{19} = \frac{-\frac{4.5 \cdot kni \cdot F_5}{(1+K)} - \alpha \cdot r}{u}$$

With the boundary conditions:

$z = 0$, $(O_2) = O_{20}$, oxygen concentration in the water column;

$z = zn$, $\dfrac{\partial O_2}{\partial z} = 0$ and $z = zn$ $(O_2) = 0$

We can write the constants:

$A_{20} = O_{20} - A_{19} - F_{16} - F_{17} - F_{18}$

$A_{19} = \dfrac{(F_{16} + F_{17} + F_{18} - O_{20}) - F_{16} \cdot e^{-\delta \cdot z_n} - F_{17} \cdot e^{a_6 \cdot z_n} - F_{18} \cdot e^{a_5 \cdot z_n} - F_{19} \cdot z_n}{e^{a_{19} \cdot z_n} - 1}$

The depth of the aerobic layer, can be determined through the resolution of:

$0 = a_{19} \cdot A_{19} \cdot e^{a_{19} \cdot z_n} - \delta \cdot F_{16} \cdot e^{-\delta \cdot z_n} + a_6 \cdot F_{17} \cdot e^{a_6 \cdot z_n} + a_5 \cdot F_{18} \cdot e^{a_5 \cdot z_n} + F_{19}$

zn>zf: If the aerobic zone is deeper than the fluid layer, the diagenetic equations can be written as:

Fluid & aerobic layer:

$$\frac{\partial O_2}{\partial t} = D_f \frac{\partial^2 O_2}{\partial z^2} - u \cdot \frac{\partial O_2}{\partial z} - \alpha \cdot \left(k1b \cdot Corg1_f + k2b \cdot Corg2_f\right) - \frac{4.5 \cdot kni}{(1+K)} \cdot NH_4(z) + \Pr odO_2 \cdot e^{-\delta z} \qquad (10)$$

Compacted & aerobic layer:

$$\frac{\partial O_2}{\partial t} = D_c \frac{\partial^2 O_2}{\partial z^2} - u \cdot \frac{\partial O_2}{\partial z} - \alpha \cdot \frac{1-\phi_c}{1-\phi_f}\left(Corg1_f \cdot k1b \cdot e^{-\frac{k1b}{w}\left(z - z_f\right)} + Corg2_f \cdot k2b \cdot e^{-\frac{k2b}{w}\left(z - z_f\right)} \right) - \frac{4.5 \cdot kni}{(1+K)} \cdot NH_4(z)$$

(11)

The solutions of equations (10) and (11) can be written as:

(10) $\left(o_2\right)_f = A_{21} \cdot e^{a_{21} \cdot z} + A_{22} + F_{20} \cdot e^{a_{13} \cdot z} + F_{21} \cdot e^{a_{14} \cdot z} + F_{22} \cdot e^{-\delta \cdot z} + F_{23} \cdot z$,

with, $a_{21} = \dfrac{u}{D_f}$, $F_{20} = \dfrac{\dfrac{4.5 \cdot kni \cdot A_{13}}{(1+K)}}{D_f \cdot a_{13}^2 - u \cdot a_{13}}$, $F_{21} = \dfrac{\dfrac{4.5 \cdot kni \cdot A_{14}}{(1+K)}}{D_f \cdot a_{14}^2 - u \cdot a_{14}}$, $F_{22} = \dfrac{\dfrac{4.5 \cdot kni \cdot F_{10}}{(1+K)} - \Pr odO_2}{D_f \cdot \delta^2 + u \cdot \delta}$,

$F_{23} = \dfrac{-\dfrac{4.5 \cdot kni \cdot F_{11}}{(1+K)} - \alpha \cdot r}{u}$

(11) $\left(o_2\right)_n = A_{23} \cdot e^{a_{23} \cdot z} + A_{24} + F_{24} \cdot e^{-\frac{k1b}{w}\left(z - z_f\right)} + F_{25} \cdot e^{-\frac{k2b}{w}\left(z - z_f\right)} + F_{26} \cdot e^{a_{15} \cdot z} + F_{27} \cdot e^{a_{16} \cdot z}$

with, $a_{23} = \dfrac{u}{D_c}$, $F_{24} = \dfrac{\alpha \cdot k1b \cdot Corg1_f \cdot \dfrac{1-\phi_c}{1-\phi_f} + \dfrac{4.5 \cdot kni \cdot F_{12}}{(1+K)}}{D_c \cdot \left(\dfrac{k1b}{w}\right)^2 + u \cdot \left(\dfrac{k1b}{w}\right)}$,

$F_{25} = \dfrac{\alpha \cdot k2b \cdot Corg2_f \cdot \dfrac{1-\phi_c}{1-\phi_f} + \dfrac{4.5 \cdot kni \cdot F_{13}}{(1+K)}}{D_c \cdot \left(\dfrac{k2b}{w}\right)^2 + u \cdot \left(\dfrac{k2b}{w}\right)}$, $F_{26} = \dfrac{\dfrac{4.5 \cdot kni \cdot A_{15}}{(1+K)}}{D_c \cdot a_{15}^2 - u \cdot a_{15}}$, $F_{27} = \dfrac{\dfrac{4.5 \cdot kni \cdot A_{16}}{(1+K)}}{D_c \cdot a_{16}^2 - u \cdot a_{16}}$

The boundary conditions are:

z = 0, $(O_2) = O_{20}$, oxygen concentration in the water column;

z=z$_f$, $\dfrac{(O_2)_n}{\phi_c} = \dfrac{(O_2)_f}{\phi_f}$, z=z$_f$, $D_c \cdot \left(\dfrac{\partial O_2}{\partial z}\right)_n = D_f \cdot \left(\dfrac{\partial O_2}{\partial z}\right)_f$

z = zn, $\dfrac{\partial O_2}{\partial z} = 0$ and z=zn $(O_2) = 0$

$$A_{23} = \frac{\dfrac{k1b}{w} \cdot F_{24} \cdot e^{-\frac{k1b}{w}\cdot\left(z_n - z_f\right)} + \dfrac{k2b}{w} \cdot F_{25} \cdot e^{-\frac{k2b}{w}\cdot\left(z_n - z_f\right)} - a_{15}\cdot F_{26}\cdot e^{a_{15}\cdot z_n} - a_{16}\cdot F_{27}\cdot e^{a_{16}\cdot z_n}}{a_{23}\cdot e^{a_{23}\cdot z_n}}$$

$$G = D_c\left(a_{23}\cdot A_{23}\cdot e^{a_{23}\cdot z_f} - \frac{k1b}{w}\cdot F_{24} - \frac{k2b}{w}\cdot F_{25} + a_{15}\cdot F_{26}\cdot e^{a_{15}\cdot z_f} + a_{16}\cdot F_{27}\cdot e^{a_{16}\cdot z_f}\right)$$

$$A_{21} = \frac{G - D_f\cdot\left(a_{13}\cdot F_{20}\cdot e^{a_{13}\cdot z_f} + a_{14}\cdot F_{21}\cdot e^{a_{14}\cdot z_f} - \delta\cdot F_{22}\cdot e^{-\delta\cdot z_f} + F_{23}\right)}{D_f\cdot\left(a_{21}\cdot e^{a_{21}\cdot z_f}\right)}$$

$$A_{22} = O_{20} - A_{21} - F_{20} - F_{21} - F_{22}$$

$$A_{24} = \frac{\varphi_c}{\varphi_f}\cdot\left(A_{21}\cdot e^{a_{21}\cdot z_f} + A_{22} + F_{20}\cdot e^{a_{13}\cdot z_f} + F_{21}\cdot e^{a_{14}\cdot z_f} + F_{22}\cdot e^{-\delta\cdot z_f} + F_{23}\cdot z_f\right)$$

$$- A_{23}\cdot e^{a_{23}\cdot z_f} - F_{24} - F_{25} - F_{26}\cdot e^{a_{15}\cdot z_f} - F_{27}\cdot e^{a_{16}\cdot z_f}$$

1.2.3 Nitrate

zn<zf: For nitrate, the diagenetic equations if aerobic layer is shallower than the fluid layer can be written as:

Fluid & aerobic layer $\dfrac{\partial NO_3}{\partial t} = D_f\dfrac{\partial^2 NO_3}{\partial z^2} - u\cdot\dfrac{\partial NO_3}{\partial z} + kni\cdot NH_4(z) - uptNO_3\cdot e^{-\delta z}$ (12)

Fluid & anaerobic layer $\dfrac{\partial NO_3}{\partial t} = D_f\dfrac{\partial^2 NO_3}{\partial z^2} - u\cdot\dfrac{\partial NO_3}{\partial z} - denit\cdot NO_3 - uptNO_3\cdot e^{-\delta z}$ (13)

Compacted & anaerobic layer $\dfrac{\partial NO_3}{\partial t} = D_c\dfrac{\partial^2 NO_3}{\partial z^2} - u\cdot\dfrac{\partial NO_3}{\partial z} - denit\cdot NO_3$ (14)

The solutions of equations (12), (13) and (14) can be written as:

(12) $(NO_3)_n = A_{26} + A_{25}\cdot e^{a_{25}\cdot z} + F_{28}\cdot e^{a_5\cdot z} + F_{29}\cdot e^{a_6\cdot z} + F_{30}\cdot e^{-\delta\cdot z} + F_{31}\cdot z$,

with $a_{25} = \dfrac{u}{D_f}$, $F_{30} = \dfrac{uptNO_3 - kni\cdot F_4}{D_f\cdot\delta^2 + u\cdot\delta}$, $F_{28} = \dfrac{-kni\cdot A_5}{D_f\cdot a_5{}^2 - u\cdot a_5}$, $F_{29} = \dfrac{-kni\cdot A_6}{D_f\cdot a_6{}^2 - u\cdot a_6}$

$F_{31} = \dfrac{kni\cdot F_5}{u}$

$$(13) \left(NO_3\right)_f = A_{27} \cdot e^{a_{27} \cdot z} + A_{28} \cdot e^{a_{28} \cdot z} + F_{32} \cdot e^{-\delta \cdot z},$$

with, $a_{27} = \dfrac{u - \sqrt{u^2 + 4 \cdot D_f \cdot denit}}{2 \cdot D_f}$, $a_{28} = \dfrac{u + \sqrt{u^2 + 4 \cdot D_f \cdot denit}}{2 \cdot D_f}$ and $F_{32} = \dfrac{uptNO_3}{D_f \cdot \delta^2 + u \cdot \delta - denit}$

$$(14) \left(NO_3\right)_c = A_{29} \cdot e^{a_{29} \cdot z}, \text{ with } a_{29} = \dfrac{u - \sqrt{u^2 + 4 \cdot D_c \cdot denit}}{2 \cdot D_c}$$

With the boundary conditions:

$z = 0$, $\left(NO_3\right)_n = NO_{30}$, oxygen concentration in the water column;

$z = z_f$, $\dfrac{\left(NO_3\right)_c}{\phi_c} = \dfrac{\left(NO_3\right)_f}{\phi_f}$, $z = z_f$, $D_c \cdot \left(\dfrac{\partial NO_3}{\partial z}\right)_c = D_f \cdot \left(\dfrac{\partial NO_3}{\partial z}\right)_f$

$z = zn$, $\left(\dfrac{\partial NO_3}{\partial z}\right)_n = \left(\dfrac{\partial NO_3}{\partial z}\right)_f$, $z = zn$, $\left(NO_3\right)_n = \left(NO_3\right)_f$

Then, $A_{26} = NO_{30} - A_{25} - F_{28} - F_{29} - F_{30}$

$$J = NO_{30} - F_{28} - F_{29} - F_{30} + F_{28} \cdot e^{a_5 \cdot z_n} + F_{29} \cdot e^{a_6 \cdot z_n} + \left(F_{30} - F_{32}\right) \cdot e^{-\delta \cdot z_n} + F_{31} \cdot z_n$$

$$A_{25} = \frac{A_{27} \cdot e^{a_{27} \cdot z_n} + A_{28} \cdot e^{a_{28} \cdot z_n} - J}{e^{a_{25} \cdot z_n} - 1}$$

$$A_{29} = \frac{D_f}{D_c \cdot a_{29} \cdot e^{a_{29} \cdot z_f}} \cdot \left(a_{27} \cdot A_{27} \cdot e^{a_{27} \cdot z_f} + a_{28} \cdot A_{28} \cdot e^{a_{28} \cdot z_f} - \delta \cdot F_{32} \cdot e^{-\delta \cdot z_f}\right)$$

$$A_{27} = \frac{A_{28} \cdot e^{a_{28} \cdot z_f} \cdot \left(-\phi_c + \dfrac{\phi_f \cdot D_f \cdot a_{28}}{D_c \cdot a_{29}}\right) - F_{32} \cdot e^{-\delta \cdot z_f} \cdot \left(\phi_c + \dfrac{\phi_f \cdot D_f \cdot \delta}{D_c \cdot a_{29}}\right)}{e^{a_{27} \cdot z_f} \cdot \left(\phi_c - \dfrac{\phi_f \cdot D_f \cdot a_{27}}{D_c \cdot a_{29}}\right)}$$

$$K = \phi_c \cdot e^{a_{27} \cdot z_f} - \frac{\phi_f \cdot D_f \cdot a_{27}}{D_c \cdot a_{29}} \cdot e^{a_{27} \cdot z_f}$$

$$L = e^{a_{28} \cdot z_f} \cdot \left(-\phi_c + \frac{\phi_f \cdot D_f \cdot a_{28}}{D_c \cdot a_{29}}\right)$$

$$M = F_{32} \cdot e^{-\delta \cdot z_f} \cdot \left(\phi_c + \frac{\phi_f \cdot D_f \cdot \delta}{D_c \cdot a_{29}}\right)$$

$$N = a_5 \cdot F_{28} \cdot e^{a_5 \cdot z_n} + a_6 \cdot F_{29} \cdot e^{a_6 \cdot z_n} - \delta \cdot \left(F_{30} - F_{32}\right) \cdot e^{-\delta \cdot z_n} + F_{31}$$

$$A_{28} = \frac{\dfrac{M \cdot e^{a_{27} \cdot z_n}}{K} \cdot \left(a_{27} - \dfrac{a_{25} \cdot e^{a_{25} \cdot z_n}}{e^{a_{25} \cdot z_n} - 1}\right) - \dfrac{J \cdot a_{25} \cdot e^{a_{25} \cdot z_n}}{e^{a_{25} \cdot z_n} - 1} + N}{a_{28} \cdot e^{a_{28} \cdot z_n} - \dfrac{a_{25} \cdot e^{a_{25} \cdot z_n} \cdot e^{a_{28} \cdot z_n}}{e^{a_{25} \cdot z_n} - 1} + \dfrac{L \cdot e^{a_{27} \cdot z_n}}{K} \cdot \left(a_{27} - \dfrac{a_{25} \cdot e^{a_{25} \cdot z_n}}{e^{a_{25} \cdot z_n} - 1}\right)}$$

zn>zf: For nitrate, the diagenetic equations if the aerobic layer penetrates deeper than the fluid layer can be written as:

Fluid & aerobic layer $\dfrac{\partial NO_3}{\partial t} = D_f \dfrac{\partial^2 NO_3}{\partial z^2} - u \cdot \dfrac{\partial NO_3}{\partial z} + kni \cdot NH_4(z) - uptNO_3 \cdot e^{-\delta z}$ (15)

Compacted & aerobic layer $\dfrac{\partial NO_3}{\partial t} = D_c \dfrac{\partial^2 NO_3}{\partial z^2} - u \cdot \dfrac{\partial NO_3}{\partial z} + kni.NH_4(z)$ (16)

Compacted & anaerobic layer $\dfrac{\partial NO_3}{\partial t} = D_c \dfrac{\partial^2 NO_3}{\partial z^2} - u \cdot \dfrac{\partial NO_3}{\partial z} - denit \cdot NO_3$ (17)

The solutions of equations (15), (16) and (17) can be written as:

(15) $(NO_3)_f = A_{32} + A_{31} \cdot e^{a_{31} \cdot z} + F_{33} \cdot e^{-\delta \cdot z} + F_{34} \cdot e^{a_{13} \cdot z} + F_{35} \cdot e^{a_{14} \cdot z} + F_{36} \cdot z$,

with $a_{31} = \dfrac{u}{D_f}$, $F_{33} = \dfrac{uptNO_3 - kni \cdot F_{10}}{D_f \cdot \delta^2 + u \cdot \delta}$, $F_{34} = \dfrac{-kni \cdot A_{13}}{D_f \cdot a_{13}^2 - u \cdot a_{13}}$, $F_{35} = \dfrac{-kni \cdot A_{14}}{D_f \cdot a_{14}^2 - u \cdot a_{14}}$

$F_{31} = \dfrac{kni \cdot F_{11}}{u}$

(16) $(NO_3)_n = A_{33} \cdot e^{a_{33} \cdot z} + A_{34} + F_{37} \cdot e^{a_{15} \cdot z} + F_{38} \cdot e^{a_{16} \cdot z} + F_{39} \cdot e^{-\frac{k1b}{w} \cdot (z - z_f)} + F_{40} \cdot e^{-\frac{k2b}{w} \cdot (z - z_f)}$

with, $a_{33} = \dfrac{u}{D_c}$, $F_{37} = \dfrac{-kni \cdot A_{15}}{D_c \cdot a_{15}^2 - u \cdot a_{15}}$, $F_{38} = \dfrac{-kni \cdot A_{16}}{D_c \cdot a_{16}^2 - u \cdot a_{16}}$, $F_{39} = \dfrac{-kni \cdot F_{12}}{D_c \cdot \left(\dfrac{k1b}{w}\right)^2 + u \cdot \left(\dfrac{k1b}{w}\right)}$ and

$F_{40} = \dfrac{-kni \cdot F_{13}}{D_c \cdot \left(\dfrac{k2b}{w}\right)^2 + u \cdot \left(\dfrac{k2b}{w}\right)}$

(17) $(NO_3)_c = A_{35} \cdot e^{a_{35} \cdot z}$, with $a_{35} = \dfrac{u - \sqrt{u^2 + 4 \cdot D_c \cdot denit}}{2 \cdot D_c}$

With the boundary conditions:
z = 0, $(NO_3)_f = NO_{30}$, oxygen concentration in the water column;

z=z$_f$, $\dfrac{(NO_3)_n}{\phi_c} = \dfrac{(NO_3)_f}{\phi_f}$, z=z$_f$, $D_c \cdot \left(\dfrac{\partial NO_3}{\partial z}\right)_n = D_f \cdot \left(\dfrac{\partial NO_3}{\partial z}\right)_f$

z = zn, $\left(\dfrac{\partial NO_3}{\partial z}\right)_n = \left(\dfrac{\partial NO_3}{\partial z}\right)_c$, z=zn, $(NO_3)_n = (NO_3)_c$

Then, $A_{32} = NO_{30} - A_{31} - F_{33} - F_{34} - F_{35}$

$P = a_{15} \cdot F_{37} \cdot e^{a_{15} \cdot z_n} + a_{16} \cdot F_{38} \cdot e^{a_{16} \cdot z_n} - \left(\dfrac{k1b}{w}\right) \cdot F_{39} \cdot e^{-\left(\frac{k1b}{w}\right) \cdot (z_n - z_f)} - \left(\dfrac{k2b}{w}\right) \cdot F_{40} \cdot e^{-\left(\frac{k2b}{w}\right) \cdot (z_n - z_f)}$

$A_{35} = \dfrac{a_{33} \cdot A_{33} \cdot e^{a_{33} \cdot z_n} + P}{a_{35} \cdot e^{a_{35} \cdot z_n}}$

$Q = F_{37} \cdot e^{a_{15} \cdot z_n} + F_{38} \cdot e^{a_{16} \cdot z_n} + F_{39} \cdot e^{-\left(\frac{k1b}{w}\right) \cdot (z_n - z_f)} + F_{40} \cdot e^{-\left(\frac{k2b}{w}\right) \cdot (z_n - z_f)}$

$$A_{34} = A_{33} \cdot e^{a_{33} \cdot z_n} \cdot \left(\frac{a_{33}}{a_{35}} - 1\right) + \frac{P}{a_{35}} - Q$$

$$R = D_f \cdot \left(-\delta \cdot F_{33} \cdot e^{-\delta \cdot z_f} + a_{13} \cdot F_{34} \cdot e^{a_{13} \cdot z_f} + a_{14} \cdot F_{35} \cdot e^{a_{14} \cdot z_f} + F_{36}\right)$$

$$S = D_c \cdot \left(a_{15} \cdot F_{37} \cdot e^{a_{15} \cdot z_f} + a_{16} \cdot F_{38} \cdot e^{a_{16} \cdot z_f} - \left(\frac{k1b}{w}\right) \cdot F_{39} - \left(\frac{k2b}{w}\right) \cdot F_{40}\right)$$

$$A_{31} = \frac{D_c \cdot a_{33} \cdot A_{33} \cdot e^{a_{33} \cdot z_f} + S - R}{D_f \cdot a_{31} \cdot e^{a_{31} \cdot z_f}}$$

$$T = \phi_c \cdot \left(F_{33} \cdot e^{-\delta \cdot z_f} + F_{34} \cdot e^{a_{13} \cdot z_f} + F_{35} \cdot e^{a_{14} \cdot z_f} + F_{36} \cdot z_f\right)$$

$$V = \phi_f \cdot \left(F_{37} \cdot e^{a_{15} \cdot z_f} + F_{38} \cdot e^{a_{16} \cdot z_f} + F_{39} + F_{40}\right)$$

$$A_{33} = \frac{\dfrac{(S-R) \cdot \phi_c}{D_f \cdot a_{31} \cdot e^{a_{31} \cdot z_f}} \cdot \left(e^{a_{31} \cdot z_f} - 1\right) + \phi_c \cdot \left(NO_{30} - F_{33} - F_{34} - F_{35}\right) + T - \dfrac{\phi_f \cdot P}{a_{35}} + \phi_f \cdot Q - V}{\phi_f \cdot e^{a_{33} \cdot z_f} + \phi_f \cdot e^{a_{33} \cdot z_n} \cdot \left(\dfrac{a_{33}}{a_{35}} - 1\right) - \dfrac{D_c \cdot a_{33} \cdot \phi_c}{D_f \cdot a_{31}} \cdot e^{(a_{33} - a_{31}) \cdot z_f} \cdot \left(e^{a_{31} \cdot z_f} - 1\right)}$$

1.2.4 Dissolved Silica

BBS>0: For both layers, providing that biogenic silica is present in the sediment, the diagenetic equations for dissolved silica can be written as:

Fluid layer: $\dfrac{\partial SDB}{\partial t} = D_f \cdot \dfrac{\partial^2 SDB}{\partial z^2} - u \cdot \dfrac{\partial SDB}{\partial z} + kd \cdot (SDB_{sat} - SDB) - uptSi \cdot e^{-\delta z}$ (18)

Compacted layer: $\dfrac{\partial SDB}{\partial t} = D_c \cdot \dfrac{\partial^2 SDB}{\partial z^2} - u \cdot \dfrac{\partial SDB}{\partial z} + kd \cdot (SDB_{sat} - SDB)$ (19)

The solutions for equation (18) and (19) are:

$$SDB_f = A_1 \cdot e^{a_1 \cdot z} + A_2 \cdot e^{a_2 \cdot z} + F_1 \cdot e^{-\delta \cdot z} + F_2, \text{ with } F_1 = \frac{uptSi}{D_f \cdot \delta^2 + u \cdot \delta - kd} \text{ and } F_2 = SDB_{sat}$$

$$SDB_c = A_{37} \cdot e^{a_{37} \cdot z} + F_2$$

With the boundary conditions:
z=0, $SDB_f = SI_0$, concentration of dissolved silica in the water column

z=z$_f$, $\dfrac{SDB_f}{\phi_f} = \dfrac{SDB_c}{\phi_c}$ and z=z$_f$, $D_f \cdot \left(\dfrac{\partial SDB}{\partial z}\right)_f = D_c \cdot \left(\dfrac{\partial SDB}{\partial z}\right)_c$

Thus,

$$A_1 = SI_0 - A_2 - F_1 - F_2$$

$$A_{37} = \frac{\phi_c}{\phi_f} \cdot e^{-a_{37} \cdot z_f} \cdot \left(A_1 \cdot e^{a_1 \cdot z_f} + A_2 \cdot e^{a_2 \cdot z_f} + F_1 \cdot e^{-\delta \cdot z_f} + F_2\right) - F_2 \cdot e^{-a_{37} \cdot z_f}$$

$$A_2 = \frac{-a_1 \cdot e^{a_1 \cdot z_f} \cdot (SI_0 - F_1 - F_2) + \delta \cdot F_1 \cdot e^{-\delta \cdot z_f} + \frac{D_c \cdot \phi_c}{D_f \cdot \phi_f} \cdot a_{37} \cdot \left(e^{a_1 \cdot z_f} \cdot (SI_0 - F_1 - F_2) + F_1 \cdot e^{-\delta \cdot z_f} + F_2\right) - \frac{D_c}{D_f} \cdot a_{37} \cdot F_2}{a_2 \cdot e^{a_2 \cdot z_f} - a_1 \cdot e^{a_1 \cdot z_f} - \frac{D_c \cdot \phi_c}{D_f \cdot \phi_f} \cdot a_{37} \cdot \left(e^{a_2 \cdot z_f} - e^{a_1 \cdot z_f}\right)}$$

BBS =0: If the biogenic silica has been dissolved, dissolved silica can be expressed as:

Fluid layer: $\dfrac{\partial SDB}{\partial t} = D_f \cdot \dfrac{\partial^2 SDB}{\partial z^2} - u \cdot \dfrac{\partial SDB}{\partial z} - uptSi \cdot e^{-\delta z}$ (20)

Compacted layer: $\dfrac{\partial SDB}{\partial t} = D_c \cdot \dfrac{\partial^2 SDB}{\partial z^2} - u \cdot \dfrac{\partial SDB}{\partial z}$ (21)

The solutions for equation (20) and (21) are:

$SDB_f = A_{43} \cdot e^{a_{43} \cdot z} + A_{44} + F_{44} \cdot e^{-\delta \cdot z}$, with $F_{44} = \dfrac{uptSi}{D_f \cdot \delta^2 + u \cdot \delta}$ and $a_{43} = \dfrac{u}{D_f}$

$SDB_c = A_{46}$

With the boundary conditions:

z=0, $SDB_f = SI_0$, concentration of dissolved silica in the water column

z=z$_f$, $\dfrac{SDB_f}{\phi_f} = \dfrac{SDB_c}{\phi_c}$ and z=z$_f$, $D_f \cdot \left(\dfrac{\partial SDB}{\partial z}\right)_f = D_c \cdot \left(\dfrac{\partial SDB}{\partial z}\right)_c$

Thus,

$A_{44} = SI_0 - A_{43} - F_{44}$

$A_{43} = \dfrac{\delta \cdot F_{44} \cdot e^{-\delta \cdot z_f}}{a_{43} \cdot e^{a_{43} \cdot z_f}}$

$A_{46} = \dfrac{\phi_c}{\phi_f}\left(A_{43} \cdot e^{a_{43} \cdot z_f} + A_{44} + F_{44} \cdot e^{-\delta \cdot z_f}\right)$

1.2.5 Dissolved phosphorus

For the fluid and compacted layers the diagenetic equations for dissolved inorganic phosphorus can be written as:

Fluid layer:

$\dfrac{\partial PO_4}{\partial t} = D_f \cdot \dfrac{\partial^2 PO_4}{\partial z^2} - w \cdot (1 + K_{PO4}) \cdot \dfrac{\partial PO_4}{\partial z} + \beta \cdot \left(k1b \cdot Corg1_f + k2b \cdot Corg2_f\right) - uptPO_4 \cdot e^{-\delta z}$ (22)

Compacted layer:

$\dfrac{\partial PO_4}{\partial t} = D_c \cdot \dfrac{\partial^2 PO_4}{\partial z^2} - w \cdot (1 + K_{PO4}) \cdot \dfrac{\partial PO_4}{\partial z} + \beta \cdot \dfrac{1 - \phi_c}{1 - \phi_f} \cdot \left(Corg1_f \cdot k1b \cdot e^{-\frac{k1b}{w}(z - z_f)} + Corg2_f \cdot k2b \cdot e^{-\frac{k2b}{w}(z - z_f)}\right)$ (23)

The solutions for equation (22) and (23) are:

$PO_{4f} = A_{47} \cdot e^{a_{47} \cdot z} + A_{48} + F_{47} \cdot e^{-\delta \cdot z} + F_{48} \cdot z$, with $a_{47} = \dfrac{w \cdot (1 + K_{PO4})}{D_f}$,

$$F_{47} = \frac{uptPO_4}{D_f \cdot \delta^2 + w \cdot (1 + K_{PO4}) \cdot \delta} \quad \text{and} \quad F_{48} = \frac{\beta \cdot r}{w \cdot (1 + K_{PO4})}$$

$$PO_{4c} = A_{50} + F_{49} \cdot e^{-\frac{k1b}{w} \cdot \left(z - z_f\right)} + F_{50} \cdot e^{-\frac{k2b}{w} \cdot \left(z - z_f\right)} + F_{51},$$

$$\text{with } F_{49} = \frac{-\beta \cdot \frac{1-\phi_c}{1-\phi_f} \cdot Corg1_f \cdot k1b}{D_f \cdot \left(\frac{k1b}{w}\right)^2 + (1 + K_{PO4}) \cdot k1b} \quad \text{and} \quad F_{50} = \frac{-\beta \cdot \frac{1-\phi_c}{1-\phi_f} \cdot Corg2_f \cdot k2b}{D_c \cdot \left(\frac{k2b}{w}\right)^2 + (1 + K_{PO4}) \cdot k2b}$$

With the boundary conditions:

z=0, $PO_{4f} = PO_{40}$, concentration of dissolved inorganic phosphorus in the water column

z=z$_f$, $\dfrac{PO_{4f}}{\phi_f} = \dfrac{PO_{4c}}{\phi_c}$ and z=z$_f$, $D_f \cdot \left(\dfrac{\partial PO_4}{\partial z}\right)_f = D_c \cdot \left(\dfrac{\partial PO_4}{\partial z}\right)_c$

Thus,

$$A_{48} = PIT_0 - A_{47} - F_{47}$$

$$A_{47} = \frac{\frac{Dc}{Df} \cdot \left(-\frac{k1b}{w} \cdot F_{49} - \frac{k2b}{w} \cdot F_{50}\right) + \delta \cdot F_{47} \cdot e^{-\delta \cdot z_f} - F_{48}}{a_{47} \cdot e^{a_{47} \cdot z_f}}$$

$$A_{48} = \frac{\phi_c}{\phi_f}\left(A_{47} \cdot e^{a_{47} \cdot z_f} + A_{48} + F_{47} \cdot e^{-\delta \cdot z_f} + F_{48} \cdot z_f\right) - F_{49} - F_{50}$$

2. Monolayer model

The model describes the distribution of all variables within an single 'fluid' layer of biofilm, of fixed thickness, including sediments trapped within an algal mat, attached to a hard, inert support.

2.1 Particulate variables

Organic carbon (Corg$_{1f}$, Corg$_{2f}$, Corg$_{3f}$), biogenic silica (BBS) and total inorganic phosphorus (PIT) are constant over the fluid layer and calculated by the main sub-model.

2.2 Dissolved variables

2.2.1 Ammonium

zn<zf: For ammonium (**NH₄**), if the aerobic layer is shallower than the fluid layer (zn<zf), the diagenetic equations for ammonium can be written as:

Fluid & aerobic layer NH4n:

$$\frac{\partial NH_4}{\partial t} = D_f \frac{\partial^2 NH_4}{\partial z} - kni \cdot NH_4 + \varepsilon \cdot \left(k1b \cdot Corg_{1f} + k2b \cdot Corg_{2f}\right) - uptNH_4 \cdot e^{-\delta z} \tag{24}$$

Fluid & anaerobic layer NH4f:

$$\frac{\partial NH_4}{\partial t} = D_f \frac{\partial^2 NH_4}{\partial z} + \varepsilon \cdot \left(k1b \cdot Corg_{1f} + k2b \cdot Corg_{2f} \right) - uptNH_4 \cdot e^{-\delta z} \tag{25}$$

The solution of equations (24) and (25) can be written as:

(24): $\left(NH_4\right)_n = A_5 \cdot e^{a_5 \cdot z} + A_6 \cdot e^{a_6 \cdot z} + F_4 \cdot e^{-\delta \cdot z} + F_5$ $\qquad$ with, $a_5 = -\sqrt{\dfrac{k_{ni}}{D_f}}$, $a_6 = \sqrt{\dfrac{k_{ni}}{D_f}}$,

$F_4 = \dfrac{uptNH_4}{D_f \cdot \delta^2 - kni}$ and $F_5 = \dfrac{\varepsilon \cdot r}{kni}$; avec $r = \left(k1b \cdot Corg_{1f} + k2b \cdot Corg_{2f} \right)$

(25): $\left(NH_4\right)_f = \dfrac{uptNH_4}{\delta^2 \cdot D_f} \cdot e^{-\delta \cdot z} - \dfrac{\varepsilon \cdot r}{2 \cdot D_f} \cdot z^2 + A_7 \cdot z + A_8$

With the boundary conditions:
z = 0, $\left(NH_4\right)_n = NH_{40}$, ammonium concentration in the water column

z = zf, $\dfrac{\partial NH_4}{\partial z} = 0$; z=zn, $\left(\dfrac{\partial NH_4}{\partial z}\right)_n = \left(\dfrac{\partial NH_4}{\partial z}\right)_f$; z=zn, $\left(NH_4\right)_n = \left(NH_4\right)_f$

Then,

$A_7 = \dfrac{uptNH_4 \cdot e^{-\delta \cdot z_f}}{\delta \cdot D_f} + \dfrac{\varepsilon \cdot r}{D_f} z_f$ $\qquad\qquad$ $A_6 = NH_{40} - A_5 - F_4 - F_5$

$A_5 = \dfrac{-\dfrac{uptNH_4 \cdot e^{-\delta \cdot z_n}}{\delta \cdot D_f} - \dfrac{\varepsilon \cdot r}{D_f} z_n + A_7 - \left(NH_{40} - F_4 - F_5\right) \cdot a_6 \cdot e^{a_6 \cdot z_n} + \delta \cdot F_4 \cdot e^{-\delta \cdot z_n}}{a_5 \cdot e^{a_5 \cdot z_n} - a_6 \cdot e^{a_6 \cdot z_n}}$

$A_8 = A_5 \cdot e^{a_5 \cdot z_n} + A_6 \cdot e^{a_6 \cdot z_n} + F_4 \cdot e^{-\delta \cdot z_n} + F_5 - \dfrac{uptNH_4}{\delta^2 \cdot D_f} \cdot e^{-\delta \cdot z_n} + \dfrac{\varepsilon \cdot r}{2 \cdot D_f} \cdot z_n^2 - A_7 \cdot z_n$

zn>zf: For ammonium (**NH₄**), if the aerobic layer is deeper than the fluid layer (zn>zf), the diagenetic equations for ammonium can be written as:

Fluid & aerobic layer:

$$\frac{\partial NH_4}{\partial t} = D_f \frac{\partial^2 NH_4}{\partial z} - kni \cdot NH_4 + \varepsilon \cdot \left(k1b \cdot Corg1_f + k2b \cdot Corg2_f \right) - uptNH_4 \cdot e^{-\delta z} \tag{26}$$

The solution of equation (26) is:
$NH_4 = A_{13} \cdot e^{a_5 \cdot z} + A_{14} \cdot e^{a_6 \cdot z} + F_4 \cdot e^{-\delta \cdot z} + F_5$ $\qquad$, with a₅, a₆, F₄ and F₅ as defined in equation (3).

The boundary conditions are:
z = 0, $NH_4 = NH_{40}$, ammonium concentration in the water column

and z = zf, $\dfrac{\partial NH_4}{\partial z} = 0$

Thus,

$A_{13} = \dfrac{\delta \cdot F_4 \cdot e^{-\delta \cdot z_f} - a_6 \cdot e^{a_6 \cdot z_f} \cdot \left(NH_{40} - F_4 - F_5\right)}{a_5 \cdot e^{a_5 \cdot z_f} - a_6 \cdot e^{a_6 \cdot z_f}}$ and $A_{14} = NH_{40} - A_{13} - F_4 - F_5$

2.2.2 Oxygen

For oxygen (O_2), the penetration depth of oxygen determines the oxic layer and the diagenetic equation can be written as:

$$\frac{\partial O_2}{\partial t} = D_f \frac{\partial^2 O_2}{\partial z^2} - \alpha \cdot \left(k1b \cdot Corg_{1f} + k2b \cdot Corg_{2f}\right) - \frac{4.5 \cdot kni}{(1+K)} \cdot NH_4(z) + \Pr odO_2 \cdot e^{-\delta z} \tag{27}$$

The solution of equation (27) is:

$$O_2 = \left(\frac{\alpha \cdot r}{2 \cdot D_f} + \frac{F_5 \cdot kni}{D_f \cdot (1+K)}\right) \cdot z^2 + \frac{4.5 \cdot kni}{D_f \cdot (1+K)}\left(\frac{A_5 \cdot e^{a_5 \cdot z}}{a_5^2} + \frac{A_6 \cdot e^{a_6 \cdot z}}{a_6^2}\right) + \frac{\left(\frac{4.5 \cdot kni \cdot F_4}{(1+K)} - \Pr odO_2\right)}{\delta^2 \cdot D_f} \cdot e^{-\delta \cdot z} + A_{19} \cdot z + A_{20}$$

With the boundary conditions:
$z = 0$, $(O_2) = O_{20}$, oxygen concentration in the water column;

$z = zn$, $\dfrac{\partial O_2}{\partial z} = 0$ and $z = zn$ $(O_2) = 0$

Thus,

$$A_{20} = O_{20} - \frac{4.5 \cdot kni}{D_f \cdot (1+K)}\left(\frac{A_5}{a_5^2} + \frac{A_6}{a_6^2}\right) - \frac{\left(\frac{4.5 \cdot kni \cdot F_4}{(1+K)} - \Pr odO_2\right)}{\delta \cdot D_f} \,,$$

$$A_{19} = -\left(\frac{\alpha \cdot r}{D_f} + \frac{4.5 \cdot F_5 \cdot kni}{D_f \cdot (1+K)}\right) \cdot z_n - \frac{4.5 \cdot kni}{D_f \cdot (1+K)}\left(\frac{A_5 \cdot e^{a_5 \cdot z_n}}{a_5} + \frac{A_6 \cdot e^{a_6 \cdot z_n}}{a_6}\right) + \frac{\left(\frac{4.5 \cdot kni \cdot F_4}{(1+K)} - \Pr odO_2\right)}{\delta \cdot D_f} \cdot e^{-\delta \cdot z_n}$$

The analytical expression of the aerobic depth (z_n) can be solved numerically and is given by the equation:

$$0 = \left(\frac{\alpha \cdot r}{2 \cdot D_f} + \frac{F_5 \cdot kni}{D_f \cdot (1+K)}\right) \cdot z_n^2 + \frac{4.5 \cdot kni}{D_f \cdot (1+K)}\left(\frac{A_5 \cdot e^{a_5 \cdot z_n}}{a_5} + \frac{A_6 \cdot e^{a_6 \cdot z_n}}{a_6}\right) + \frac{\left(\frac{4.5 \cdot kni \cdot F_4}{(1+K)} - \Pr odO_2\right)}{\delta \cdot D_f} \cdot e^{-\delta \cdot z_n} + F_{16} \cdot z_n + F_{17}$$

If the aerobic layer covers the fluid layer, zn=zf.

2.2.3 Nitrate

zn<zf: For nitrate (NO_3), if the aerobic layer is shallower than the fluid layer (zn<zf), the diagenetic equations for nitrate can be written as:

Fluid & aerobic layer $\quad \dfrac{\partial NO_3}{\partial t} = D_f \dfrac{\partial^2 NO_3}{\partial z^2} + kni \cdot NH_4(z) - uptNO_3 \cdot e^{-\delta z}$ \hfill (28)

Fluid & anaerobic layer $\quad \dfrac{\partial NO_3}{\partial t} = D_f \dfrac{\partial^2 NO_3}{\partial z^2} - denit \cdot NO_3 - uptNO_3 \cdot e^{-\delta z}$ \hfill (29)

The solution of the diagenetic equations (28) and (29) are:

$$\left(NO_3\right)_n = -\frac{kni}{D_f}\left(\frac{A_5 \cdot e^{a_5 \cdot z}}{a_5^{\,2}} + \frac{A_6 \cdot e^{a_6 \cdot z}}{a_6^{\,2}} + \frac{F_5}{2}z^2\right) + \frac{\left(uptNO_3 - kni \cdot F_4\right)}{\delta^2 \cdot D_f}\cdot e^{-\delta \cdot z} + A_{25}\cdot z + A_{26}$$

$$\left(NO_3\right)_f = A_{27}\cdot e^{a_{27}\cdot z} + A_{28}\cdot e^{a_{28}\cdot z} + F_{32}\cdot e^{-\delta \cdot z}\ , \text{ with, } a_{27} = -\sqrt{\frac{denit}{D_f}}\ ,\quad a_{28} = \sqrt{\frac{denit}{D_f}} \text{ and}$$

$$F_{32} = \frac{uptNO3}{D_f \cdot \delta^2 - denit}$$

With the boundary conditions:

$z = 0$, $\left(NO_3\right) = NO_{30}$, nitrate concentration in the water column;

$z = zf$, $\dfrac{\partial NO_3}{\partial z} = 0$, $z=zn$ $\left(\dfrac{\partial NO_3}{\partial z}\right)_n = \left(\dfrac{\partial NO_3}{\partial z}\right)_f$ and $z=zn$ $\left(NO_3\right)_n = \left(NO_3\right)_f$

Thus,

$$A_{26} = NO_{30} + \frac{kni}{D_f}\left(\frac{A_5}{a_5^{\,2}} + \frac{A_6}{a_6^{\,2}}\right) - \frac{\left(uptNO3 - kni \cdot F_4\right)}{\delta^2 \cdot D_f}$$

$$A_{27} = \frac{-F_{32}\cdot e^{-\delta \cdot z_f} - a_{28}\cdot A_{28}\cdot e^{a_{28}\cdot z_f}}{a_{27}\cdot e^{a_{27}\cdot z_f}}$$

$$A_{25} = A_{28}\left(a_{28}\cdot e^{a_{28}\cdot z_n} - \frac{a_{27}\cdot e^{a_{27}\cdot z_n}\cdot a_{28}\cdot e^{a_{28}\cdot z_f}}{a_{27}\cdot e^{a_{27}\cdot z_f}}\right) - \frac{a_{27}\cdot e^{a_{27}\cdot zn}\cdot F_{32}\cdot e^{-\delta\cdot z_f}}{a_{27}\cdot e^{a_{27}\cdot z_f}} - \delta\cdot F_{32}\cdot e^{-\delta\cdot z_n}$$
$$+ \frac{kni}{D_f}\left(\frac{A_5\cdot e^{a_5\cdot z_n}}{a_5} + \frac{A_6\cdot e^{a_6\cdot z_n}}{a_6} + F_5\cdot z_n\right) + \frac{e^{-\delta\cdot z_n}}{\delta\cdot D_f}\left(uptNO3 - kni\cdot F_4\right)$$

$$A_{28} = \frac{\left(\dfrac{a_{27}\cdot e^{a_{27}\cdot z_n}\cdot F_{32}\cdot e^{-\delta\cdot z_f}}{a_{27}\cdot e^{a_{27}\cdot z_f}} + \delta\cdot F_{32}\cdot e^{-\delta\cdot z_n} + \dfrac{kni}{D_f}\left(\dfrac{A_5\cdot e^{a_5\cdot z_n}}{a_5} + \dfrac{A_6\cdot e^{a_6\cdot z_n}}{a_6} + F_5\cdot z_n\right) + \dfrac{e^{-\delta\cdot z_n}}{\delta\cdot D_f}\left(uptNO3 - kni\cdot F_4\right)\right)\cdot z_n}{\left(a_{28}\cdot e^{a_{28}\cdot z_n} - \dfrac{a_{27}\cdot e^{a_{27}\cdot z_n}\cdot a_{28}\cdot e^{a_{28}\cdot z_f}}{a_{27}\cdot e^{a_{27}\cdot z_f}}\right)\cdot z_n + \dfrac{e^{a_{27}\cdot z_n}\cdot a_{28}\cdot e^{a_{28}\cdot z_f}}{a_{27}\cdot e^{a_{27}\cdot z_f}} - e^{a_{28}\cdot z_n}}$$
$$\frac{-A_{26} + F_{32}\cdot e^{-\delta\cdot z_n} + \dfrac{kni}{D_f}\left(\dfrac{A_5\cdot e^{a_5\cdot z_n}}{a_5^{\,2}} + \dfrac{A_6\cdot e^{a_6\cdot z_n}}{a_6^{\,2}} + \dfrac{F_5}{2}\cdot z_n^2\right) - \dfrac{e^{-\delta\cdot z_n}}{\delta^2\cdot D_f}\left(uptNO3 - kni\cdot F_4\right)}{}$$

zn=zf: For nitrate, if the aerobic layer covers the fluid layer, the diagenetic equation for nitrate can be written as:

$$\frac{\partial NO_3}{\partial t} = D_f\frac{\partial^2 NO_3}{\partial z^2} + kni\cdot NH_4(z) - uptNO_3\cdot e^{-\delta z} \tag{30}$$

The solution of equation (30) can be written as:

$$\left(NO_3\right) = -\frac{kni}{D_f}\left(\frac{A_{13}\cdot e^{a_5\cdot z}}{a_5^{\,2}} + \frac{A_{14}\cdot e^{a_6\cdot z}}{a_6^{\,2}} + \frac{F_5}{2}z^2\right) + \frac{\left(uptNO_3 - kni\cdot F_4\right)}{\delta^2\cdot D_f}\cdot e^{-\delta\cdot z} + A_{31}\cdot z + A_{32}$$

With the boundary conditions:

$z = 0$, $(NO_3) = NO_{30}$, nitrate concentration in the water column;

$z = zf$, $\dfrac{\partial NO_3}{\partial z} = 0$

Thus,

$$A_{32} = NO_{30} + \frac{kni}{D_f}\left(\frac{A_{13}}{a_5{}^2} + \frac{A_{14}}{a_6{}^2}\right) - \frac{(uptNO3 - kni \cdot F_4)}{\delta^2 \cdot D_f}$$

$$A_{31} = \frac{kni}{D_f}\left(\frac{A_{13} \cdot e^{a_5 \cdot z_f}}{a_5} + \frac{A_{14} \cdot e^{a_6 \cdot z_f}}{a_6} + F_{11} \cdot z_f\right) + \left(\frac{uptNO3 - kni \cdot F_{10}}{\delta \cdot D_f}\right) \cdot e^{-\delta \cdot z_f}$$

2.2.4 Silica

For dissolved silica (**SDB**), providing that biogenic silica is present in the sediment, the diagenetic equation can be written as:

$$\frac{\partial SDB}{\partial t} = D_f \cdot \frac{\partial^2 SDB}{\partial z^2} + kd \cdot (SDB_{sat} - SDB) - uptSi \cdot e^{-\delta z} \tag{31}$$

The solution of equation (31) can then be written as:

$$SDB = A_1 \cdot e^{a_1 z} + A_2 \cdot e^{a_2 z} + F_1 \cdot e^{-\delta z} + F_2 \quad \text{with,} \quad a_1 = -\sqrt{\frac{k_d}{D_f}}, \quad a_2 = \sqrt{\frac{k_d}{D_f}}, \quad F_1 = \frac{uptSi}{D_f \cdot \delta^2 - kd} \quad \text{and}$$

$F_2 = SDB_{sat}$

Using the boundary conditions at:

$z = 0$, $(SDB)_0 = Si_0$, dissolved silica concentration in the water column

$z = z_f$, $\dfrac{\partial SDB}{\partial z} = 0$

The two boundary conditions allow the determination of the constant:

$$A_1 = Si_0 - A_2 - F_1 - F_2 \qquad\qquad A_2 = \frac{\delta \cdot F_1 \cdot e^{-\delta \cdot z_f} - a_1 \cdot e^{a_1 \cdot z_f} \cdot (Si_0 - F_1 - F_2)}{a_2 \cdot e^{a_2 \cdot z_f} - a_1 \cdot e^{a_1 \cdot z_f}}$$

Providing that biogenic silica has been totally dissolved, the diagenetic equation for dissolved silica can be written as:

$$\frac{\partial SDB}{\partial t} = D_f \cdot \frac{\partial^2 SDB}{\partial z^2} - uptSi \cdot e^{-\delta z} \tag{32}$$

The solution of equation (32) can be written as:

$$SDB = \frac{uptSi \cdot e^{-\delta z}}{\delta^2 \cdot D_f} + A_{43} \cdot z + A_{44}$$

The boundary conditions are the same than for equation (32), thus:

$$A_{43} = \frac{uptSi \cdot e^{-\delta \cdot z_f}}{\delta \cdot D_f} \qquad A_{44} = Si_0 - \frac{uptSi}{\delta^2 \cdot D_f}$$

2.2.5 Dissolved phosphorus

For the fluid layer the diagenetic equation for dissolved inorganic phosphorus can be written as:

$$\frac{\partial PO_4}{\partial t} = D_f \cdot \frac{\partial^2 PO_4}{\partial z^2} + \beta \cdot \left(k1b \cdot Corg1_f + k2b \cdot Corg2_f \right) - uptPO_4 \cdot e^{-\delta z} \qquad (33)$$

The solution for equation (33) is:

$$PO_{4f} = -\frac{r \cdot \beta}{2 \cdot D_f} \cdot z^2 + \frac{uptPO4}{\delta^2 \cdot D_f} \cdot e^{-\delta \cdot z} + A_{51} \cdot z + A_{52}, \qquad \text{with} \qquad F_{51} = \frac{uptPO_4}{D_f \cdot \delta^2 + k_{des}} \qquad \text{and}$$

$$F_2 = \frac{k_{des} \cdot PO_{4eq} - \beta \cdot r}{k_{des}}$$

With the boundary conditions:

z=0, $PO_{4f} = PO_{40}$, concentration of dissolved inorganic phosphorus in the water column

and z=z_f, $\left(\dfrac{\partial PO_4}{\partial z} \right)_f = 0$

Thus,

$$A_{52} = PIT_0 - \frac{uptPO4}{\delta^2 \cdot D_f}$$

$$A_{52} = \frac{r \cdot \beta}{D_f} \cdot z_f + \frac{uptPO4}{\delta \cdot D_f} \cdot e^{-\delta \cdot z_f}$$

5. Conclusion

Le sous-modèle benthique représentant les processus de diagénèse précoce du sédiment de fond de rivière ou de lac développé lors de ces travaux a été conceptualisé dans l'optique d'être intégré à un modèle de transport-réaction dans la colonne d'eau (appelé ici le modèle principal). Ce modèle déterministe est basé sur la conception du continuum aquatique au sein duquel les processus affectant la qualité de l'eau sont identiques, seules les contraintes extérieures varient (température, lumière, quantités et qualité des sédiments déposées ou érodées, production primaire et concentration des variables dissoutes dans la colonne d'eau)

L'originalité de notre modèle benthique réside dans le fait qu'il représente entièrement les processus biogéochimiques interdépendant intervenant dans les transformations du carbone organique, de l'oxygène, de l'ammonium, du nitrate, des phosphate et de la silice dissoute. Il permet de traiter des situations diverses rencontrées le long d'un continuum aquatique grâce au modèle principal qui lui fournira les concentrations en carbone organique déposées à la surface du sédiment ainsi que la hauteur de la couche fluide, selon les processus de déposition/érosion dans la colonne d'eau.

La nécessité d'intégrer notre modèle benthique à ce modèle principal a conduit à certaines hypothèses simplificatrices : état stationnaire, représentation du continuum sédimentaire par un 2 couches discontinues, concentration homogène des variables solides dans le sédiment superficiel. Toutefois, malgré ces hypothèses, nous avons montré que le modèle est capable de représenter correctement les flux de matières dissoutes (oxygène, ammonium, nitrate et phosphate) et les profils de concentration dans le sédiment (carbone organique, ammonium, nitrate et phosphate) pour trois sites étudiés (bassin de rétention de Méry s/Oise, La Seine à Porcheville et le ruisseau Orneau en Belgique), couvrant une large diversité de situations en termes de flux de sédimentation de matières solides et de composition de ces matières déposées. Le modèle est donc susceptible d'être utilisé tout au long du continuum aquatique.

L'analyse de sensibilité aux principaux facteurs de forçages que nous avons réalisée illustre la multiplicité des interactions prises en compte au sein de ce sous-modèle benthique, et la complexité de la réponse du système. Le modèle mono-couche n'a pas pu être testé entièrement dans cette étude, toutefois les résultats présentés lors de l'analyse de sensibilité nous montrent la cohérence de ce modèle et l'intérêt de le tester de manière plus approfondie.

Ces travaux ont abouti à l'écriture d'un article en anglais intitulé « Modelling nutrient exchange at the sediment – water interface of River Systems », que nous allons soumettre au journal Ecological modelling en septembre 2005. Cet article présente la structure du modèle ainsi que les équations diagénétiques utilisées. Les résultats cohérents de son application à trois études de cas nous permettent de penser que ce modèle est suffisamment robuste pour être intégrer dans un modèle de transport/réaction dans la colonne d'eau. L'étape suivante du travail consistera donc à intégrer notre modèle benthique au sein du modèle SENECAM développé par Ruelland et Billen (2005), et à tester le comportement de l'ensemble, d'abord sur des cas fictifs idéalisés (cours d'eau linéaire de caractéristiques morphologiques et hydrologiques données), puis sur des cas réels documentés expérimentalement.

Le projet ambitieux que nous poursuivons, au delà du présent travail de Master, est en effet de réaliser un modèle d'ensemble des processus affectant la qualité de l'eau au sein d'un réseau hydrographique. Ce modèle sera appliqué sur une rivière finlandaise lors de la suite de ma thèse au sein de l'Université des Technologies de Helsinki (HUT).

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