Relations between bacterial biomass and carbon cycle in marine sediments :

An early diagenetic model

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Abstract

A new model for early diagenetic processes has been developed through a new formulation explicitly accounting for a microbial population dynamics. Following a mechanistic approach based on enzymatic reactions, a new model has been proposed for oxic mineralisation and denitrification. It incorporates dynamics of bacterial metabolism. We find a general formulation for inhibition processes for which some of other mathematical relations are particular cases.

Moreover a fast numerical algorithm has been developed. It allows us to perform simulations of different diagenetic models in non steady states. We use this algorithm to compare our model to a classical one (Soetaert *et al*, 1996). Dynamical evolutions since a perturbation of particulate organic carbon (POC) input are studied for both models.

The results are very similar for stationary cases. But with variable inputs, the bacterial biomass dynamics brings about noticeable differences, which are discussed.

Introduction

Different physical, chemical and biological processes modify organic matter deposited on the sediments. Those, which act up to thousand years, are called early diagenetic processes. Any estimation of the fluxes of organic matter in the ocean is based on the quantification of the early diagenetic processes. Indeed, when deposited on the sediment, the organic matter can be trapped definitely in the sediment in some cases and its degradation speed depends on the processes involved.

Among the diagenetic processes, the present paper focuses mainly on the modelling of the microbiological ones. In the sediment column, there are some oxic microniches in the anoxic layer. Bacteria degrade the organic matter via different metabolisms that depend on the physical and chemical sediment properties. The rupture of the oxygen gradient has thus a direct effect on the processes used by bacteria to alter the organic matter, by inducing RedOx oscillations, which in turn will change the global degradation rate. As a consequence, the quantification of these processes and their interactions provides a better understanding of the different chemical compounds dynamics in the sediments.

We aim to analyse the dynamics of diagenetic processes in sediment submitted to perturbations. These perturbations may be either natural (phytoplanktonic bloom) or the result of human activities (oil spill). It is the reason why we explicitly take the biological compartments into account since any perturbation should modify living communities, which in turn have different responses in their function with respect to their environment. In this paper:

- we present a mechanistic diagenetic model where the formulation of biological processes is based on bacterial metabolisms, which involve enzymatic

processes; in order to keep a rather simple model at the ecosystem level, we use quasi-steady state assumptions on the enzymatic processes;

- we propose an advanced numerical program (in FORTRAN 90) to perform simulations; this program allows us to make simulations of the diagenetic system of a few months in a few minutes; this implies that we can study the impact of different perturbations scenarios (non-steady states).

These points provide the basis of a theoretical background for the study of perturbations of the benthic environment. In this paper, we only deal with two processes: oxic mineralisation and denitrification. This choice is based on the two following reasons : (*i*) we need at least two different electrons acceptors to analyse the interaction of two bacterial metabolisms, (*ii*) we want to work with the simplest model and oxic mineralisation associated with denitrification are the main processes at the short time scale (few months) in the first centimetres of sediment. Nitrification is a process associated to oxic mineralisation and consequently, an extra term is added to describe the effect of nitrification on the amount of nitrate.

In the following section, we recall some generalities on usual diagenetic models in order to explain where our approach is different and why it can be useful. The third section concerns our new model description. The fourth section is devoted to the numerical scheme. Finally, we compare two models (with and without bacterial biomass dynamics) and discuss the results.

Diagenetic models

Early diagenetic models (Berner, 1980; Soetaert *et al*., 1996; Boudreau, 1996, 1997) provide quantification of fluxes and reaction rates based on measured profiles in different sediments. Usually based on the Berner's diagenetic equation (1980), they are

the most employed models for the benthic system. This equation, applying to solute as well as solid species, is a partial differential equation (PDE) incorporating physical transport processes and biogeochemical reactions. Its mathematical formulation appears under the following general shape:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - W\frac{\partial C}{\partial z} - \Sigma R \qquad (1.1)$$

Time variation = *Diffusion* + *Advection* + *Reaction;*

with C the tracer concentration, D the diffusion coefficient, W the advection velocity and $\sum R$ the biogeochemical reactions rates.

- Diffusion process allows local transport of matter from a point to another one with random motion (Crank, 1976). This coefficient includes biodiffusion, bioirrigation and molecular diffusion effects.

- Advection is an environmental bulk transport with the velocity W; it is the expression of different physical processes like (*i*) burial linked with particles sedimentation at the sediment interface (W sedimentation velocity) (Goldberg and Koide, 1962; Guinasso and Schink, 1975; Benninger *et al*., 1979; Fisher *et al*., 1980; Aller and DeMaster, 1984; etc.), (*ii*) compaction which corresponds to a reduction of sediment volume under the action of overlying sedimentary column weights (W is then the particles or interstitial water movement resulting of this phenomenon) (Berner, 1980; Boudreau, 1997), (*iii*) advection phenomena linked to benthic organisms activity like the one gathered in “non-local” transport of “conveyor-belt” organisms (Fisher *et al*., 1980; Robbins, 1986; Rice *et al*., 1986; Boudreau, 1997).

- Reaction term describes (*i*) kinetics of the different compounds (organic matter, oxygen, nitrate, manganese, etc.) via biochemical reactions, (*ii*) sinks and sources of “non-local” transport model as sediment ingestion by conveyor-belt organisms or as irrigation (Boudreau, 1997).

Berner' s equation is the basis of more complex and more realistic models. For instance, Soetaert (*et al*., 1996) proposes a model with two types of organic matter (with different lability) which are submitted to transport (diffusive and advective) and biochemical reactions (oxic mineralisation, denitrification, etc.). This model is applied in different types of marine sediments, such as deep and coastal environments. In this kind of model, attention is paid on the sequence of different biochemical reactions in the sediment according to a gradient of decreasing oxygen concentration with respect to depth.

However, in many works, the impact of microbial organisms is not sufficiently taken into account. More precisely, only a few models investigate the relations between bacterial biomass and organic carbon in biogeochemical models (see for instance Boudreau, 1999 in the sediments or Anderson and Williams, 1999 in the column water). Generally, the models do not explicitly take into account the dynamics of bacterial community. The assumption of steady state for bacterial populations densities is implicitly made, which supposes that bacteria are always present. It leads to relative simple biochemical terms in the models, which is very useful according to the complexity induced by the large number of involved processes.

Classically, the biochemical processes have the following form (Rabouille and Gaillard, 1991, Soetaert *et al*., 1996; Boudreau, 1996):

$$OM = \frac{R_{Min} O_2 C}{K_{s,M} + O_2} \qquad \text{for oxic mineralisation} \tag{1.2}$$

$$Denit_S = \frac{R_{Dénit} NO_3 C}{K_{s,D} + NO_3}\left(1 - \frac{O_2}{O_2 + K_{Inhib}}\right) \text{ for denitrification} \tag{1.3}$$

with $\begin{cases} R_{Dénit}, R_{Min} : \text{maximum degradation rate for organic carbon} \\ K_{s,M} : \text{half-saturation constant for oxygen limitation in oxic mineralization} \\ K_{s,D} : \text{half-saturation constant for nitrate limitation in denitrification} \\ K_{inhib} : \text{half-saturation constant for oxygen inhibition in denitrification} \end{cases}$

The inhibition of denitrification induced by the oxygen is described by the mean of a decreasing function with respect to oxygen concentration. This function is based on empirical arguments which formulation depends on the authors. For instance, Rabouille (*et al*., 2001) has drawn up denitrification process on the following way:

$$Denit_R = \frac{R_{\max}^{NO_3} NO_3 C}{K_{m\,NO_3} + NO_3} \exp\left[-\left(\frac{O_2}{K_{m\,O_2}}\right)^2\right] \tag{1.4}$$

with $\begin{cases} R_{\max}^{NO_3} : \text{maximum oxidation rate of the organic mater by NO3} \\ K_{m\,O_2} : \text{Monod constant for oxygen diminution} \\ K_{m\,NO_3} : \text{Monod constant for nitrate consumption} \end{cases}$

These examples show that the biochemical part are usually based on a Michaelis-Menten kinetics, possibly associated to an inhibition factor in case of competition between different electrons acceptors. For the both denitrification process formulations, $Denit_S$ and $Denit_R$, it can be noted that the inhibition term is large when oxygen concentration increases, keeping the denitrification rate low.

The stationary state assumption for bacterial biomass leads to some theoretical limitations. Natural (phytoplanktonic bloom) or anthropic (hydrocarbon layer)

perturbations of the environment will cause disturbances in living communities governing diagenetic processes; dynamical mineralisation will be modified in return. Moreover, some bioturbation processes (Boudreau, 1986) lead to aerobic microniches creation in anaerobic sediment (Fenchel, 1996). These oxygenation modifications lead to a transfer between redox area, a re-oxidation process and redox oscillations increase, inducing a recombining of bacterial communities and thus a modification of bacterial metabolisms. Modelling microbial dynamics in relation with bioturbation is then important to understand the environment evolution.

Microbial activities modelling

Degradation rates

We propose here a new mathematical model for the sedimentary diagenetic processes, based on Berner's diagenetic equation (1980). Our formulation incorporates physical processes and biogeochemical reactions realised by bacteria. It takes explicitly bacterial dynamics into account. We will describe differences between a classical model composed of biogeochemical reactions developed by Soetaert (*et al*., 1996) and our new model. This comparison will be made in the numerical results section.

Our interest turns on vertical distribution in the first centimetres of sediment column for dissolved oxygen, solid organic carbon (POC), dissolved nitrate and bacterial biomass. Reaction terms of our model are obtained from enzymatic mechanisms of oxic mineralisation and denitrification chemical reactions.

Concerning the nitrification process, we only deal with the nitrification associated to oxic mineralisation, resulting from the transformation of produced ammonium to nitrate. For the sake of simplicity, we have decided to avoid inserting the extra variable corresponding to the concentration of ammonium. Indeed, it supposes a complete and

instantaneous transformation of ammonium produced by oxic mineralisation. Thus, in order to keep rather closed to the real set of processes, we have considered the nitrification kinetics proportional to the mineralisation one. The proportionality coefficient is denoted γ_N and we will explain this part more precisely later on.

The way we use to build the oxic mineralisation rate is a common way in biochemistry, but it is rarely developed in biogeochemical works. Since we use the same way for building the denitrification rate, we recall the method here.

The chemical reaction associated to oxic mineralisation could be described schematically by:

$$C_{Org} + O_2 + \theta_f \xrightarrow[k]{} C\theta_u \xrightarrow[k']{} C_{Min} + P_1 + \theta_f \tag{1.5}$$

Organic carbon C_{org} can be split up to mineral carbon C_{min}. Available enzymes can belong to two states free or used. The amounts of used and free enzymes are denoted θ_u and θ_f respectively. A temporary enzymatic complex $C\theta_u$ is formed during the reaction. P_1 symbolises the reduced anoxic mineralisation products released by enzymes at the end of degradation sequence. *k* and *k'* are the reactivity rates.

The oxygen kinetics, which gives the oxic mineralisation rate, is given by:

$$\frac{dO_2}{dt} = -kO_2C\theta_f \tag{1.6}$$

according to the Mass Action Law. The equation of temporal evolution for θ_f resulting of (1.6) could be written as:

$$\frac{d\theta_f}{dt} = -kO_2C\theta_f + k'C\theta_u \tag{1.7}$$

Let $\theta = \theta_f + \theta_u$, (1.7) becomes:

$$\frac{d\theta_f}{dt} = -kO_2C\theta_f + k'C\left(\theta - \theta_f\right) \tag{1.8}$$

Considering the time scales differences between enzymatic processes and biogeochemical processes, the stationary hypothesis of the total enzymes number at short time scale could be done. It means, that at the geochemical time scales, $\frac{d\theta_f}{dt} = 0$ (Quasi Steady State assumption), and thus:

$$\theta_f = \frac{k'\theta}{k' + kO_2} \tag{1.9}$$

Entering θ_f value in equation (1.6), we find:

$$\frac{dO_2}{dt} = -\frac{k'\theta kO_2}{k' + kO_2}C = -\frac{k'\theta O_2}{\frac{k'}{k} + O_2}C = -\frac{R_{Min}O_2}{K_{s,M} + O_2}C \tag{1.10}$$

It is the classical form of Michaelis model of the equation (1.2) with $R_{Min} = k'\theta$ and $K_{s,M} = \frac{k'}{k}$.

As for oxic mineralisation, we consider the enzymatic reaction for denitrification process. In this case, enzymes react preferentially with oxygen. A system of two reactions is needed to describe the complete enzymatic reaction of organic carbon degradation:

$$C_{Org} + NO_3 + \theta_f \xrightarrow[k_1]{} C\theta_u \xrightarrow[k_1']{} C_{Min} + P_2 + \theta_f \tag{1.11}$$

$$C\theta_u + O_2 \xrightarrow[k_2]{} NO_3 + C_{Min} + P_3 + \theta_f \tag{1.12}$$

This set of reactions could be described by the following system of differential equations:

$$\frac{dNO_3}{dt} = -k_1\, NO_3\, C\, \theta_f + k_2\, C\, O_2 \theta_u \tag{1.13}$$

$$\frac{d\theta_f}{dt} = -k_1\, NO_3\, C\, \theta_f + k_1'\, C\, \theta_u + k_2\, C\, \theta_u O_2 \tag{1.14}$$

Assuming a constant global concentration of enzymes $\theta = \theta_f + \theta_u$ at short time scale (Quasi Steady State Assumption) that is the stationary state of equation (1.14):

$$\theta_f = \theta \frac{k_1' + k_2\ O_2}{k_1\, NO_3 + k_1' + k_2\ O_2} \tag{1.15}$$

Entering this result in equation (1.13):

$$\begin{aligned} \frac{dNO_3}{dt} &= -k_1\, NO_3\, C\, \theta \frac{k_1' + k_2\ O_2}{k_1\, NO_3 + k_1' + k_2\ O_2} + k_2\, C\, O_2 \theta \left(1 - \frac{k_1' + k_2\ O_2}{k_1\, NO_3 + k_1' + k_2\ O_2}\right) \\ &= C\,\theta \left(-k_1\, NO_3 \frac{k_1' + k_2\ O_2}{k_1\, NO_3 + k_1' + k_2\ O_2} + k_2\ O_2 \frac{k_1\, NO_3}{k_1\, NO_3 + k_1' + k_2\ O_2}\right) \\ &= C\,\theta k_1\, NO_3 \frac{-k_1'}{k_1\, NO_3 + k_1' + k_2\ O_2} \end{aligned} \tag{1.16}$$

The inhibition role of oxygen can be seen through its denominator place. To compare this result to Soetaert (*et al.*, 1996) proposal (equation (1.3)) – a classical michaelian form with an inhibition function - equation (1.16) can be written as:

$$\begin{aligned} \frac{dNO_3}{dt} &= -C\theta \frac{k_1' NO_3}{\frac{k_1'}{k_1} + NO_3} \left(1 - \frac{O_2}{\frac{k_1}{k_2} NO_3 + \frac{k_1'}{k_2} + O_2}\right) \\ &= -C \frac{R_{Denit}\, NO_3}{K_{s,D} + NO_3} \left(1 - \frac{O_2}{K_{Inhib} + O_2}\right) \end{aligned} \tag{1.17}$$

K_{Inhib} is no more a constant but a linear function of NO_3.

$$K_{Inhib} = \frac{k_1}{k_2} NO_3 + \frac{k_1'}{k_2} \tag{1.18}$$

$$\text{and} \begin{cases} R_{Denit} = k_1' \theta \\ K_{s,D} = \frac{k_1'}{k_1} \end{cases}$$

As a conclusion, we find a denitrification rate rather closed to that used by Soetaert (*et al.*, 1996) in which the inhibition 'constant' is no more constant but is nitrate dependent. This method provides a mechanistic basis to the denitrification rate used in our biogeochemical model. Moreover, finding the usual model through this enzymatic degradation process allows showing the biological phenomena evident role in these diagenetic processes.

Bacterial Biomass

We add a variable for the bacterial biomass, which should be related to the amount of available enzymes θ. In the present work, for the sake of simplicity, we assume that the total amount of available enzymes is proportional to bacterial biomass B:

$$\theta = EB \tag{1.19}$$

This relation is assumed in the present work. Indeed a good description of the bacterial growth rate should use an energy budget model to get a relationship between metabolic activities and bacterial population growth (Kooijman, 1996). This is the topic of a future work. Furthermore, in this paper, to keep as simple as possible, we assume a logistic growth of bacterial population, with intrinsic growth rate and carrying capacity as functions of substrates (carbon, oxygen and nitrate). Indeed, we assume that the intrinsic growth rate is proportional to consumed substrates: the more bacteria are

active, the more they duplicate. The carrying capacity is supposed to be proportional to available carbon resource, qualifying substrate availability and its accessibility by the biomass density. A simple differential equation based on these assumptions is:

$$\begin{cases} \dfrac{dB}{dt} = \alpha_{Bac}\left(OM + Denit\right)B\left(1 - \dfrac{B}{K_B}\right) \\ K_B = \gamma_B C \end{cases} \tag{1.20}$$

The coefficient α_{Bac} traduces the bacteria population production rate according to the resource. When α_{Bac} = 1, this production rate is maximal and the bacteria profile will be almost proportional to the POC one's (with γ_B as proportionality coeficient). We choose α_{Bac} = 0.3 (see table 1 and fig. 3) because this value seems to be more realistic (Goldman and Dennett, 2000).

Complete model

We propose a model, which extends usual ones in the sense that it described explicitly the bacterial biomass. Moreover, we realised the model in such way that if the bacterial biomass is maintained to a constant value then we get a usual formulation. In other words, if:

$$B\left(t, z\right) = 1 \tag{1.21}$$

then our reaction terms are identical to Soetaert ones (*et al*., 1996) in the limit of the studied processes.

Reaction part depends on bacteria number, so that without bacteria, organic components will not be degraded. Moreover, bacteria do not have their own motion; adsorbed to sediment particles, they will be moved with sediment.

In our case, porosity is considered to be constant. This relation is used to rely dissolved and particular elements:

$$\frac{\text{vol particle}}{\text{vol dissolved}} = \frac{1-\phi}{\phi} \tag{1.22}$$

where ϕ is porosity.

A four state variables model based on Berner's equation and describing for particular organic carbon (noted *C*), oxygen, nitrate and bacteria population dynamics is realised. It contains spatial variation of dynamical fields, our proposed reaction terms for oxic mineralisation and denitrification and a bacteria growth term.

$$\begin{cases} \dfrac{\partial C}{\partial t} = -\dfrac{\partial w_C C}{\partial z} + \dfrac{\partial}{\partial z}\left(D_C \dfrac{\partial C}{\partial z} \right) - \dfrac{R_{Min} O_2}{K_{s,M} + O_2} BC - \dfrac{R_{Denit} NO_3}{K_{s,D} + NO_3}\left(1 - \dfrac{O_2}{K_{Inhib} + O_2} \right) BC \\ \dfrac{\partial O_2}{\partial t} = -\dfrac{\partial w_{O_2} O_2}{\partial z} + \dfrac{\partial}{\partial z}\left(D_{O_2} \dfrac{\partial O_2}{\partial z} \right) - \gamma_{Min}\left(\dfrac{1-\phi}{\phi} \right) \dfrac{R_{Min} O_2}{K_{s,M} + O_2} BC \\ \dfrac{\partial NO_3}{\partial t} = -\dfrac{\partial w_{NO_3} NO_3}{\partial z} + \dfrac{\partial}{\partial z}\left(D_{NO_3} \dfrac{\partial NO_3}{\partial z} \right) + \left(\dfrac{1-\phi}{\phi} \right)\left(\gamma_N \dfrac{R_{Min} O_2}{K_{s,M} + O_2} - \gamma_{Denit} \dfrac{R_{Denit} NO_3}{K_{s,D} + NO_3}\left(1 - \dfrac{O_2}{K_{Inhib} + O_2} \right) \right) BC \\ \dfrac{\partial B}{\partial t} = -\dfrac{\partial w_B B}{\partial z} + \dfrac{\partial}{\partial z}\left(D_B \dfrac{\partial B}{\partial z} \right) + \alpha_{Bac} B\left(1 - \dfrac{B}{K_B} \right)\left(\dfrac{R_{Min} O_2}{K_{s,M} + O_2} + \dfrac{R_{Dénit} NO_3}{K_{s,D} + NO_3}\left(1 - \dfrac{O_2}{K_{Inhib} + O_2} \right) \right) C \end{cases} \tag{1.23}$$

where $R_{Min} = k^{'}$, $R_{Denit} = k_1^{'}$, K_{Inhib} is a linear function of nitrogen, K_B a linear function of POC and α_{Bac} is the transformation rate of POC in bacterial biomass (the growth efficiency). In this study, we consider spontaneous nitrification reaction of the ammonium, produced by oxic mineralisation process. The ammonium transformation induces a nitrate increase with the rate γ_N.

Numerical schemes

In order to look for an approached solution of proposed mathematical models, we choose finite volume method. Each part of equations is integrated on a small volume CV (control volume) where computed values are supposed constant. With Ostogradsky theorem, volumes integrals can be changed into surfaces integrals on CV faces (Ferzinger *et al.*, 1999) and equation type of the system becomes:

$$\int_V \frac{\partial C}{\partial t} dv + \int_S \left(C\vec{w}\right)\vec{n} ds - \int_S \left(\beta D_z \frac{\partial C}{\partial z}\vec{z}\right)\vec{n} ds - \sum \int_V R(C) dv = 0 \qquad (1.24)$$

where $\vec{n}$ is the normal vector trough-outer oriented; CVs are based on Cartesian 2D mesh (node centred) with irregular steps. Each CV face is labelled with its cardinal direction (just North and South in our 1D case).

This efficient computation method also adds the benefit to integrate naturally the mass conservation equation.

For spatial discretisation, the simplest but accurate method of midpoint rule is used for approximation of surface integrals. For example, the integral of the value *f* at a North cell face is:

$$F_n = \int_{Sn} f dS = \overline{f_n} S_n \approx f_n S_n \qquad (1.25)$$

The same low-level approximation is used for volumes integrals and the value of the integral of q is Vq_p where V is the CV volume and q_p the value of q at the CV centre. To approximate values at CV faces, we use linear interpolation between the two nearest nodes.

The interpolation for diffusive flux is also based on the assumption of a linear profile between two consecutive CV centres and, for example, the spatial gradient of *C* at the North face is:

$$\left(\frac{\partial C}{\partial z}\right)_n \approx \frac{C_N - C_P}{z_N - z_P} \tag{1.26}$$

P points out the present node; lowercase is used for faces and uppercase for nodes.

Boundary conditions are the particular values given to each equation of the system at the frontiers of modelled space. These conditions must be well defined for existence and uniqueness therefore for numerical simulations. If the concentration is given at the boundary, it's a Dirichlet condition; if the spatial concentration gradient is given at the boundary, it's a Neumann condition. To represent POC input, mostly dominated by bioturbation effects, a Neumann condition is used. For dissolute elements (oxygen and nitrogen), concentration at water-sediment interface is defined by a Dirichlet condition.

For finite volumes method, if the boundary of simulated domain express a physical impermeability for an element, it's not necessary to define a boundary condition (advection and diffusion fluxes are null). For bacteria population, we choose to consider no sink or source from surface, so no fluxes were calculated through the CV face of surface.

For numerical diffusion, instability problems or computational cost, it's sometime interesting to compute separately each different term of the convection-diffusion equation with a well appropriate temporal scheme. Douglas (1956), Peaceman and Rachford (1955) proposed this splitting-up idea in first. An explicit method is used for the non-linear reaction terms while a more accuracy implicit method is used for the transport equation. This splitting-up method can only be used with small disturbances

hypothesis, which means that dynamical fields have small local variations on time and space.

For one equation:

$$\begin{cases} \int_V \frac{\partial C}{\partial t} dv + \int_S (Cw\underline{z})\underline{n} ds - \int_S \left(\beta D_z \frac{\partial C}{\partial z} \underline{z} \right) \underline{n} ds = 0 \\ \int_V \frac{\partial C}{\partial t} dv - \sum \int_V R(C) dv = 0 \end{cases} \tag{1.27}$$

Consequently, we consider separately the transport terms and the reactions terms in the equations system. First, the time dependent equations of reaction terms are calculated and secondly, this partial result is applied for the transport terms to find the global result at the next time-step. We obtain for the explicit and implicit Euler method:

$$\begin{cases} C^{n+1*} = \frac{\Delta t}{V} \sum \int_V R\left(C^n\right) dv + C^n \\ C^{n+1} = \frac{\Delta t}{V} \left[\int_S \left(\beta D_z \frac{\partial C^{n+1}}{\partial z} \underline{z} \right) \underline{n} ds - \int_S \left(C^{n+1} w \underline{z} \right) \underline{n} ds \right] + C^{n+1*} \end{cases} \tag{1.28}$$

where we used the shorthand notation $C^{n+1} = C\left(t_n + \Delta t\right)$ and the * indicates that is not the final value of the solution at t_{n+1}.

To dismiss stability and excessive numerical diffusion problems, we choose an implicit resolution method to solve the system of linear equation of transport. However, to realise a lot of tests, we need to use accuracy iterative methods like GMRES or bi-CGSTAB as propose Van den Vorst (1992). We used the Fortran 90 library "smlib v1.1" for sparse matrix calculations created by Meese (1998), which proposes routines for these iterative methods. Based on these tools, which compute only non-zero elements, we have realised accuracy routine for products of sparse matrix, systems of linear equation resolution and matrix inversion in our models.

Simulations and Numerical results

Steady State

One-dimensional simulations are realised in a sedimentary column of 30 centimetres. A 200 nodes grid with constant steps of 0.5 millimetres on the first 8 centimetres and increasing for the rest is used.

We consider sediment porosity (ϕ) and temperature (T) constant throughout sedimentary column (ϕ = 0.8, T= 15°C). Solute oxygen and nitrogen diffusion coefficients (respectively D_{O2} and D_{NO3}) - corresponding to molecular diffusion and bioirrigation, depending on biodiffusion – are also constant in the surface layer of sedimentary column (6 first centimetres). Their values are calculated by Soetaert (*et al*., 1996) from sediment temperature and porosity, coefficient for temperature dependency of diffusion coefficient and molecular diffusion coefficient at 0°C of these compounds. We assume sediment bulk constant. Particles sedimentation rate is considered constant during time and throughout sedimentary column (W = 1cm/10$years$).

All the compounds values, their dynamical fields and associated reactions are resumed in the following table.

Table 1: state variables and parameters

Our study consists in a comparison of two models. The first one, so-called MODEL I, does not take explicitly into account bacterial biomass and is obtained from (1.23) where the bacterial biomass is maintained fixed at a unit value $B(z,t) \equiv 1$. It corresponds to usual types of models. The second model (MODEL II) is that we developed in this paper and is actually given by equations (1.23). We start from a steady state configuration where almost compounds are degraded and simulate a perturbation. Then we analyse the impact of taking the bacterial biomass explicitly into account via the

responses of the different solutes concentrations to the perturbations. As a consequence, we first research a stationary state with constant input of chemical elements (POC, O_2 and NO_3) at the surface. Even if only a few parts of early diagenetic processes are modelled here, realistic numerical values are used.

The coefficient K_B, which defines the maximum bacteria number locally present in the sedimentary column, depends linearly on POC concentration (equation 1.20). The largest the coefficient of proportionality γ_B, the more will grow the bacteria number in the environment and the more mineralisation processes are important. An analyse of the effect of this parameter γ_B on the bacterial biomass at steady state and on the POC quantity is presented on figure 2. γ_B value is chosen to have for the both steady state models the same quantity of POC in the sedimentary column.

Figure 1: γ_B influence

In order to have a reference for the comparison between MODEL I and MODEL II, we started with the same global mass of POC for both models at steady state, which is obtained by putting γ_B = 2.52E-04. The result is presented in figure 2.

Figure 2: steady state profiles comparison

Vertical profiles, at steady state, obtained with both models, are shown on figure 2. Starting from the water-sediment interface, POC is degraded by O_2 and an exponential decreasing of these elements could be observed. The NO_3 concentration is increased by the nitrification at the surface. . Mostly important differences can be seen for oxygen and nitrate profiles. Model 2 use globally a less quantity of electron acceptor for degrading the same POC quantity.

With defined compounds surface inputs and bacteria grow coefficients, steady vertical profiles, where almost elements concentration disappear, are obtained (see

figure 2). The differences between both models are coming from vertical repartition of bacteria. Assuming that model I is similar to model II if state variable B is fixed at 1, comparisons between models are possible. At this steady state, model II bacteria profile is almost proportional to POC one's. This repartition, mostly important in the surface layer, activates oxic mineralisation effects. With a weak quantity of biomass, model II carry similar results.

Figure 3: Bacteria profile

Perturbations

Starting from the precedent stationary state, a perturbation in POC input is applied. This is a theoretical perturbation where the amount of available carbon flux at the water-sediment interface is doubled. We aim to understand the bacterial variable response to an increased input at the surface. On figure 4 are shown the profiles dynamics for both models simultaneously; the outline resulting from the MODEL I simulation are represented in solid line while that obtained with MODEL II is in dashed line The number of each outline corresponds to the number of evolution day starting from the initial perturbation. The high differences for POC concentrations are the consequence of the response of bacterial biomass to POC flux increase.

Figure 4: both models profiles comparison

The POC is half-degraded in the first centimetres upward layer. The system needs a long time to come back to a steady state, which is not yet reached after more than 1000 days for the MODEL I. The oxygen concentration decreases fast and anoxic conditions reach the 2 centimetres layer after a month. When the new equilibrium state is approached, the sediment is anoxic after 1 centimetre deep. Nitrogen concentration starts to vanish in the both models only after few days when POC penetrate in a weakly

oxic layer. The nitrogen peak concentration comes near the surface to settle down at 2 millimetres deep.

Even if, both models have similar trends, for MODEL II, POC concentration burying is very limited and a new equilibrium state seems to be reach faster.

Figure 5: bacteria evolution

The bacterial biomass dynamics follows that of POC concentration. This increasing biomass has an important influence POC disappearance. These simulations show a problem with our mathematical model formulation since, even when there are no electron acceptors, bacterial biomass is still important. This artefact can be avoided by adding terms corresponding to biomass loss (maintenance, mortality). This will be done in a future work.

Figure 6 presents the strength of the biogeochemical processes, oxic mineralisation and denitrification, that are taken into account in the models presented in this paper. Both models are presented on the same figure for comparison. Once again, we can see the role of the extra variable associated to bacterial biomass. Indeed, it can be seen that the oxic mineralisation process is exacerbated and denitrification process is reduced in MODEL II with respect to MODEL I. The deposition of organic matter leads to an intense bacterial production, which in turn is translated into these higher biogeochemical activities. This mineralisation activity leads to a nitrate production and an activity peak of denitrification at to millimetre deep.

Figure 6: reactions intensity comparison between models

Finally, we end this comparison with that of the matter assessment on the whole sediment column. This step should be important in practice since it concerns the role of modelling. Indeed, this type of models is often used to calculate assessment in order to know, for instance, if the sediment is a source or a sink of carbon, nitrogen, and so on.

The results are presented on figure 7. We can see that the POC quantities are very different for both models. However, we can also note that the significant differences for oxygen and nitrogen concentrations at the start of the perturbation vanish with compounds disappearance. The proportional increasing of bacteria biomass accorded to the resource guard the sediment column against POC buries.

Figure 7: Assessment amounts comparison

Conclusion

We presented a diagenetic model where the bacterial biomass is explicitly taken into account. We built the model on a mechanism based on enzymatic processes. We then obtained the model at the global scale by using time scales arguments and the quasi-steady state assumption. Dilão and Domingos (2000) suggested this method to build trophic chains; we show here that this approach is even more powerful and is useful to build general ecosystem models on mechanistic arguments. This method is a particular case of the aggregation of variables method described in Auger and Poggiale (1998) for example.

We have shown that the model without explicit bacterial biomass gives significant differences in the dynamics of the profiles as in the assessments. We shall resume three points, which we consider as important in our approach. First of all, we note that the added particulate organic carbon is fast degraded in bacteria are taken into account: when the environment is enriched, the bacterial biomass is enhanced in the upper sediment layer. This phenomenon can not be simulated by model I which exhibits an organic matter burial in deeper layers. The second point concerns the processes intensities (oxic mineralisation and denitrification). Simulations show that the former is enhanced at the sediment surface with model II while the latter is reduced. This can be

the result of the strong activity due to large bacterial biomass in the oxic zone. Since the POC is fast consumed, the deeper layer is poorer with respect to organic matter and thus the denitrification intensity is smaller. In model I, since the bacterial biomass is constant, the added carbon is burying and transported in anoxic zone where it is denitrified. This remark is corroborated by the nitrate profile simulated by both models: model I exhibits a low nitrate concentrations profile with respect to model II. The last point deals with the assessments simulation: we see that the POC amount in the sediment is much larger in model I than in model II. This is the result of the previous points. However, we must say that there is no bacterial biomass loss in our model. This loss should in fact be a source of POC and a more complete model should give a lower difference in the assessment.

From a numerical point of view, considering diffusion and convection rates, use of an implicit temporal scheme was not necessary, but these simulations had allowed testing the computational speed and quality of results relatively to time and space steps. Finite volume method seems to be well appropriate for this kind of modelling. The program was created for simulate easily each diagenetic model based on Berner equation and this first use is satisfactory. The program can realise 2D simulation too, and simulations of dynamical evolutions around macrobenthos perturbation will be tested – for these cases, the efficiency of the chosen numerical discretisation could be tested.

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Caption of table and figures

Table 1: state variables and parameters - recapitulative table of notation, units, description and initial value of state variables and parameters used in the MODELS I and II.

Figure 1: γ_B influence - analysis of the effect of proportionality coefficient γ_B, included in the expression of the carrying capacity K_B (equation 1.20), on the bacterial biomass at steady state and on the POC quantity.

Figure 2: steady state profiles comparison - vertical steady state profiles comparison of POC, O_2 and NO_3 between the MODEL I (in solid line) and the MODEL II (in dashed line) with the same global mass of POC ($\gamma_B = 0.024$).

Figure 3: Bacteria profile - vertical bacterial biomass profile with model II (dashed line) compared with POC profile (solid line). At steady state, both profiles are proportional. As a reference, a vertical straight line indicates the value of bacterial biomass assumed by model I.

Figure 4: both models profiles comparison - profiles evolution comparison of POC, O_2 and NO_3 concentrations between the both models. The outline, resulting from the model I simulation, is represented in solid line and in dashed line the profile evolutions of model II. The number associated to each outline corresponds to the number of evolution day since the initial perturbation.

Figure 5: Bacteria profile evolution – profiles of bacteria for model II compared with POC profiles evolution

Figure 6: reactions intensity comparison between models - strength comparison of the biogeochemical processes (oxic mineralisation and denitrification) between the MODEL I (in solid line) and the MODEL II (in dashed line). The number associated to each outline corresponds to the number of evolution day since the initial perturbation.

Figure 7: Assessment amounts comparison - temporal evolution comparison of POC, O_2 and NO_3 amounts in the whole sedimentary column between the MODEL I (in solid line) and the MODEL II (in dashed line). The bacterial biomass of the MODEL II has been multiplied by 4 to adjust its outline to the POC one's.

Table 1

Notation	Units	Description	value
		State Variables	
C	$\mu mol.l^{-1}d^{-1}$	Particulate Organic Carbon (POC) concentration (surface concentration for stationary state)	9000
O_2	$\mu mol.l^{-1}$	Oxygen concentration (surface)	130
NO_3	$\mu mol.l^{-1}$	Nitrate concentration (surface)	20
B	%	Bacteria number	-
		Parameters	
Physical and numerical geometry			
z_{max}	cm	Maximum depth of the sedimentary column	30
N	number	Grid number	300
Δz	cm	space step (for first 8 cm)	0.05
Δt	d	Time step	0.001
Physical fields and constants			
W	$cm.d^{-1}$	Sedimentation velocity	1cm/10 yr.
D_{O2}	$cm^2.d^{-1}$	Global diffusion coefficient for oxygen (0 - 6 cm)	3.0
D_{NO3}	$cm^2.d^{-1}$	Global diffusion coefficient for nitrogen (0 - 6 cm)	2.7
$D_{M\,O2}$	$cm^2.d^{-1}$	Molecular diffusion coefficient for oxygen	1.0
$D_{M\,NO3}$	$cm^2.d^{-1}$	Molecular diffusion coefficient for nitrogen	0.9
ϕ	%	Porosity	0.8
Biological			
$D_B\,D_C$	$cm^2.d^{-1}$	Global Biodiffusion coefficient for bacteria and POC (0 - 6 cm)	0.05
α_{Bac}	$l.(\mu mol\ C)^{-1}$	Transformation rate of POC in bacterial biomass	0.3
γ_B	$\%.(\mu mol\ C)^{-1}$	proportionality coefficient to POC for environment capacity of bacteria	2.52E-04
Biogeochemical			
R_{Min}, $R_{Dénit}$	d^{-1}	Maximum degradation rate of POC in coastal area for oxic mineralisation and denitrification	0.04
$K_{s,\,M}$	$\mu mol\ O_2.l^{-1}$	Half-saturation constant (HSC) for O_2 limitation in oxic mineralisation	3
$K_{s,\,D}$	$\mu mol\ NO_3.l^{-1}$	HSC for NO_3 limitation in denitrification	30
K_{Inhib}	$\mu mol\ O_2.l^{-1}$	HSC for O_2 inhibition in denitrification	10
γ_{Min}	$mol\ O_2.(mol\ C)^{-1}$	Mol O_2 used per mol of POC in oxic mineralisation	1
γ_D	$mol\ NO_3.(mol\ C)^{-1}$	Mol NO_3 used per mol of POC in denitrification	0.8
γ_N	$mol\ NO_3.(mol\ O_2)^{-1}$	Mol NO_3 create per mol of O_2 in nitrification	.14

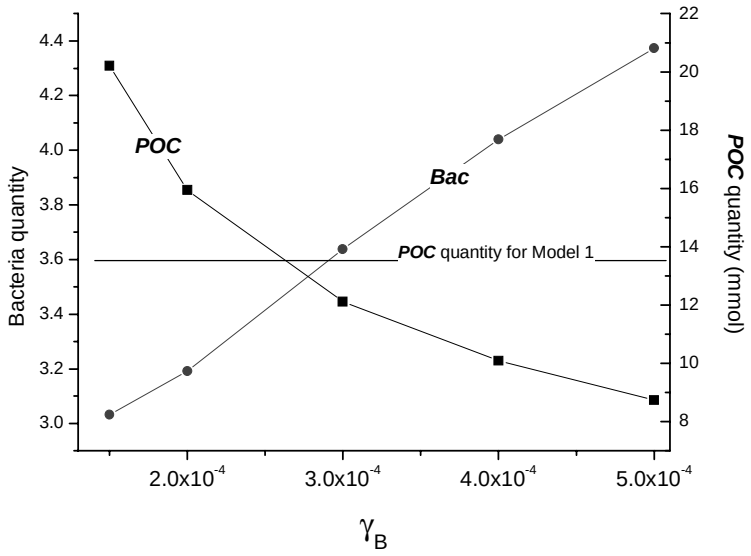


Figure 1

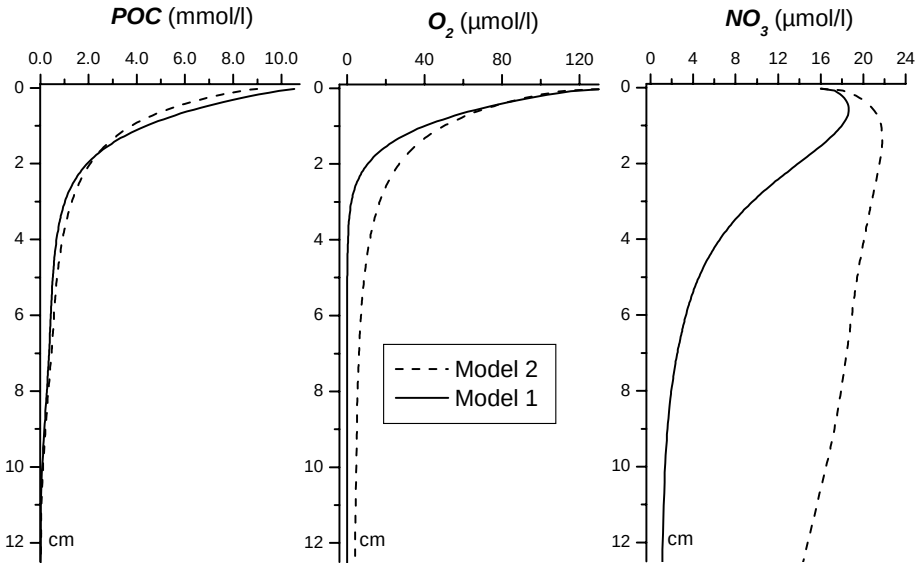
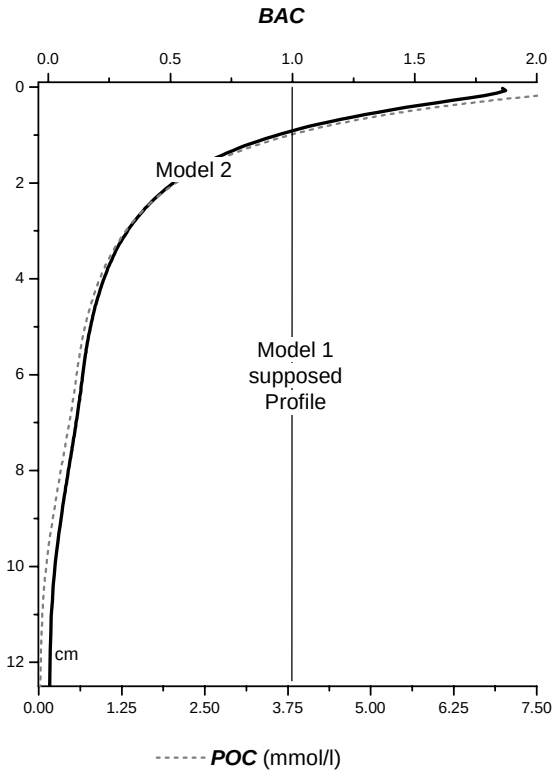


Figure 2



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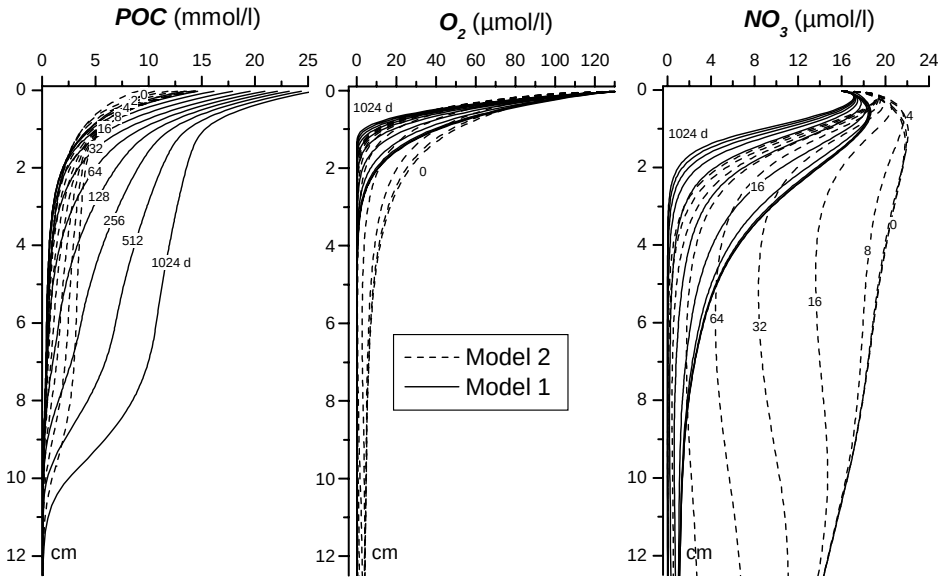

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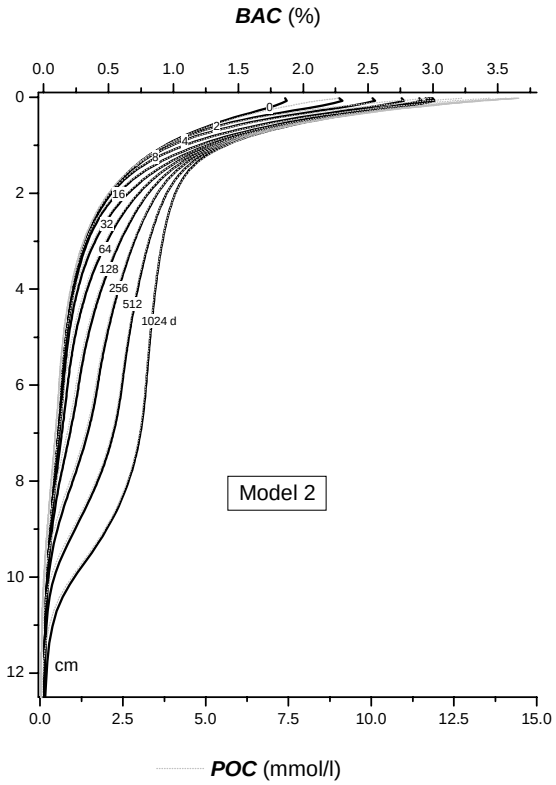

Figure 5

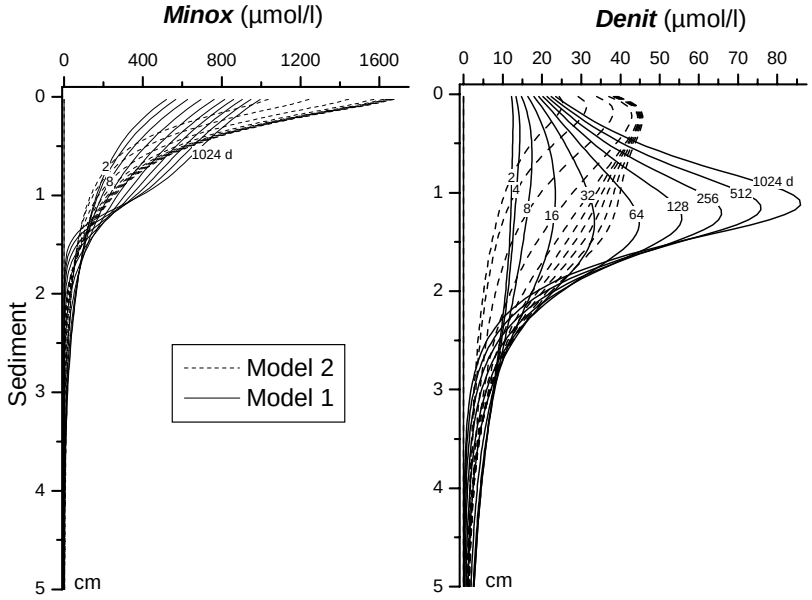

Figure 6

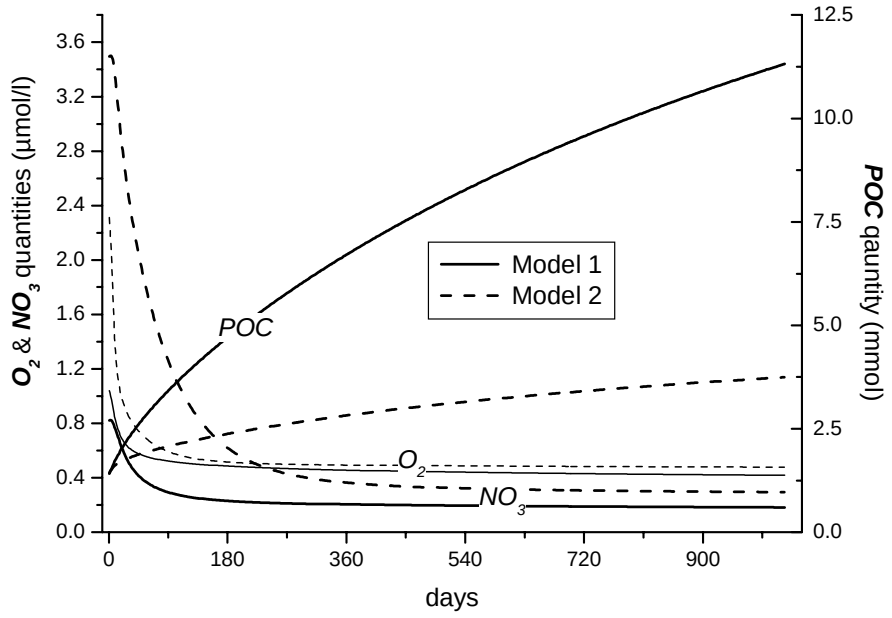
O2 & NO3 quantities (µmol/l)
POC qauntity (mmol)
days
Model 1
Model 2
POC
O2
NO3
0.0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6
0.0
2.5
5.0
7.5
10.0
12.5
0
180
360
540
720
900

Figure 7