

Simulation of O₂, PO₄ and organic carbon behavior during a benthic chamber experiment on the deep-sea floor

Early diagenesis
Organic carbon
Oxygen
Benthic chamber
Diagenetic model

Diagenèse précoce
Carbone organique
Oxygène
Chambre benthique
Modèle diagénétique.

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ABSTRACT

Using a time-dependent model for organic matter mineralization by oxygen and the resulting phosphate production in deep-sea sediments, the progress of a benthic chamber experiment is simulated. Assuming a known steady state as starting condition, the vertical distribution of chemical species in the sediments, pore water and solids, and the concentrations in the benthic chamber are calculated. Compared to previous approaches, the computation scheme utilized here considers explicitly a coupled and non-linear kinetic formulation of organic carbon oxidation and oxygen reduction. The purpose of this modeling approach is to assess the validity of conventional interpretations of benthic chamber experimental data.

The results of the calculations show that the concentration gradients of solutes at the sediment-water interface and the penetration depth of O₂ in the sediment undergo important changes during the deployment of a benthic chamber. On the contrary, the particulate phase distribution (organic carbon) is only slightly modified.

The model is further used to perform numerical experiments and the different techniques used to calculate fluxes (linear regression, zero-order model) are compared. Differences exist between the different ways of calculating the chemical fluxes. It is shown that a systematic bias, ranging from 10 to 20 %, is introduced by the linear regression technique. On the other hand, calculations performed with a simple zero-order model agree within 2 to 5 % with our calculations and therefore provide a very good estimate of the solute fluxes.

RÉSUMÉ

Simulation du comportement de l'oxygène, des phosphates et du carbone organique pendant le déploiement d'une chambre benthique sur les fonds océaniques.

Le déploiement d'une chambre benthique a pu être simulé à l'aide d'un modèle représentant la minéralisation de la matière organique par l'oxygène et la production de phosphates dissous qui en résulte. En partant d'un état stationnaire connu, la distribution verticale des espèces chimiques dissoutes et particulaires et les variations de concentration dans la chambre benthique ont été calculées. Par rap-

port aux approches précédentes, le schéma de calcul utilisé ici admet explicitement que la cinétique d'oxydation du carbone organique et la réduction de l'oxygène sont non-linéaires et couplées. Le but de cet article est de déterminer le degré de validité des différentes méthodes conventionnelles de calcul des flux benthiques. En outre, les expériences numériques nous permettent de définir les conditions idéales de temps et de concentration pour une estimation optimale des flux avant un déploiement effectif.

Les résultats des calculs montrent que les gradients de concentration des solutés à l'interface eau-sédiment subissent de profonds changements ainsi que la profondeur de pénétration de l'oxygène. A l'inverse, la répartition de la phase particulaire (carbone organique) n'est que légèrement modifiée.

Le résultat de nos expériences numériques est ensuite utilisé comme un jeu de données et les flux sont recalculés par la technique d'ajustement linéaire ou par d'autres méthodes de calcul des flux. Les écarts entre les différentes manières de calculer les flux sont examinés et nous montrons qu'un biais systématique de 10 à 20 % est introduit par la méthode de la régression linéaire. D'autre part, les calculs effectués avec un modèle simple d'ordre zéro sont en accord à 2-5 % près avec nos propres calculs et, par conséquent, ils représentent une estimation raisonnable du flux d'oxygène.

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INTRODUCTION

The sediment-water interface is a very reactive site for particles in the deep sea, because their residence time in surficial sediments is much greater than their sinking time in the water column (Lerman, 1979). The material reaching at the sea floor is subsequently degraded at this interface by numerous bacterial communities for which it constitutes the only food supply. Organic matter is particularly affected by these transformations. One part is mineralized and returns to the ocean and another part is buried (Reimers and Suess, 1983). The precise knowledge of the fractions which are mineralized or buried is of great importance in assessing the role of the sedimentary environment in the global carbon cycle on geological time-scales (Bernier, 1982; Bernier, 1991; Sundquist, 1985).

In surficial sediments of the open ocean, an important fraction of the particulate organic carbon input is degraded by aerobic bacteria (Bender and Heggie, 1984). These communities consume oxygen diffusing from the overlying water and produce CO₂, inorganic nitrogen compounds, phosphate and other metabolites as the result of their activity.

In this regard, the determination of benthic fluxes of dissolved nutrients and oxygen serves to quantify the regeneration rates in the sediments near the interface. Mass balances can then be computed with estimates of settling particulate flux, burial fluxes and mineralization rates.

Partition between the buried and mineralized fractions of this particulate organic matter rain can therefore be estimated.

During the past decade, benthic fluxes of oxygen and nutrients have been measured in the deep-sea environment through the use of benthic chambers (Smith, 1974) or incubations (Pamatmat, 1971), or estimated using pore water profiles. The first section of this paper contains a brief description of the different techniques allowing flux measurements in the deep-sea.

An important problem in estimating benthic fluxes is the fact that sediment and pore water compositions change according to incubation conditions and fluxes vary due to non-steady state conditions. The region of the sediment affected mostly by these changes is the layer situated just below the sediment-water interface. This layer actually controls the instantaneous value of the flux.

Hence, the question addressed in this paper concerns the validity of the estimation of benthic fluxes calculated after benthic chamber experiments. As the real value of the benthic flux must be extrapolated from such an experiment, it is important to assess the errors associated with the different methods of interpreting the time series measurements.

In order experimentally to check the variation of the sediment composition during a chamber deployment, it would be necessary to follow the time evolution of different solute profiles in the sediment pore waters. This is hardly feasible *in situ*, in deep-sea conditions, and we chose to address this question through a modeling approach. Therefore, we have designed a time-dependent model which is an extension of the model of Rabouille and Gaillard (1991). This model represents the organic matter transformation in the oxic part of the sediment. It computes oxygen, metabolizable organic carbon, and phosphate profiles as a function of time during the simulated deployment of a benthic chamber.

Using the data generated by a simulation, it is possible to compare the fluxes obtained using different fitting techniques.

We were able to test the assumptions of a recent, but simpler model (Hall *et al.*, 1989) used for interpreting oxygen benthic chamber measurements. This zero-order model states that the rate of oxygen utilization is proportional to the depth of O₂ penetration in the sediment, and that the oxygen profile at each time step is at steady-state.

The measurement of solute fluxes across the sediment-water interface

Indirect measurements

Solute fluxes across the sediment-water interface may be estimated using measurements of the concentration gradients of the solutes at the sediment-water interface. The flux across the interface is expressed as follows (Sayles, 1979; and others):

$$F_{\text{sol}}^{\text{SWI}} = \phi D_{\text{sol}}^{\text{sed}} \left. \frac{dC_{\text{sol}}}{dx} \right|_{z=0} + \phi \omega C_{\text{sol}}^{z=0} \quad (1)$$

$F_{\text{sol}}^{\text{SWI}}$: Flux of the solute through the sediment-water interface.

$D_{\text{sol}}^{\text{sed}}$: Diffusion coefficient in the sediment of the dissolved component.

ϕ : Porosity.

ω : Advection rate at the sediment-water interface.

$C_{\text{sol}}^{z=0}$: Concentration of the solute at the sediment-water interface.

$\left. \frac{dC_{\text{sol}}}{dx} \right|_{z=0}$: Concentration gradient at the sediment-water interface.

Generally, the advection flux ($\phi \omega C_{\text{sol}}^{z=0}$) is insignificant compared to the diffusive flux and is neglected in most of the environments which are not subject to external flow. Estimating chemical fluxes through the sediment-water interface using this approach depends critically on the resolution of the measured profile. This has led to the design of close interval samplers for interstitial water, such as the whole core squeezer of Bender *et al.* (1987), or to *in situ* measurements of microprofiles for oxygen (Reimers, 1987) and pH (Archer *et al.*, 1990). Furthermore, calculations that consider only diffusive transport neglect phenomena occurring at the sediment-water interface itself, *e.g.* the existence of a layer containing a high proportion of labile organic matter, such as the fluff layer (Lampitt, 1985; Lochte and Turley, 1988), or transport mechanisms occurring on a larger scale than the coring, such as bio-irrigation in the margin areas (Emerson *et al.*, 1984; Rutgers van der Loef *et al.*, 1984).

Direct measurements

At the same time, the scientific community has developed devices that provide *in situ* estimates of solute fluxes through the sediment-water interface. The principle of benthic chamber operation is to incubate a well defined sediment surface area surmounted by a known enclosed volume of sea water in which concentration changes are measured as a function of time (Fig. 1). The variations of concentrations in the chamber are the result of uptake of oxidants by the sediment (Smith, 1978; Hall *et al.*, 1989; Jahnke *et al.*, 1990 and others) or the release of metabolites (Devol, 1987; Anderson *et al.*, 1986; Berelson *et al.*, 1990; Jahnke, 1990 and others). The chamber requires sufficient stirring to homogenize the enclosed volume and prevent the formation of concentration gradients. The stirring is also required to mimic the natural turbulence present at the sediment-water interface. This is particularly important when diffusion of solutes through the diffusive sublayer may be the limiting mode of mass transfer. It is therefore mandatory to tune the stirring adequately.

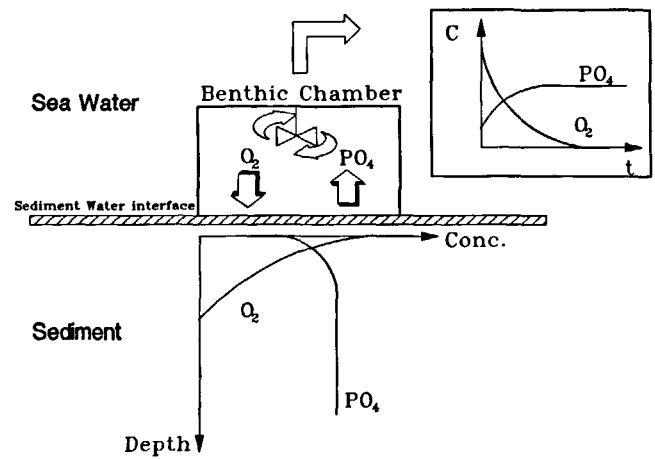


Figure 1

General diagram showing a benthic chamber deployed on the sea floor with the sediment below. Schematic concentrations of PO_4 and O_2 in the sediment and their variation in the benthic chamber are also displayed.

Diagramme général montrant une chambre benthique déployée sur les fonds océaniques. Les concentrations schématiques de O_2 et de PO_4 dans le sédiment et leurs variations dans la chambre benthique sont également tracées.

In the deep sea, Smith and co workers (1976, 1983) have used a Free Vehicle Grab Respirometer (FVGR) to measure the oxygen consumption and the nutrient release of the sediment. The MANOP group has developed a sophisticated free-vehicle benthic chamber to measure radio tracer uptake and nutrient regeneration on the sea floor (Weiss *et al.*, 1977; Bender, 1983; Santschi *et al.*, 1983). This system was designed as a closed environment with four chambers and allowed tracer injection. A Swedish group working on coastal sediments (Rutgers van der Loef *et al.*, 1984; Anderson *et al.*, 1986), used benthic chambers that were operated by divers and followed the long-term evolution of the sediments under oxic and anoxic conditions. Recently, simpler and reliable devices have been designed to perform solute flux measurements, *in situ*, in deep-sea sediments (Berelson and Hammond, 1986; Devol, 1987; Jahnke and Christiansen, 1989). The devices can operate either as closed or as open systems. The open system technique consists in balancing the loss of water drawn in the sampler by an equal amount of bottom water, whereas the closed system uses volume compensation. These devices use different sampling techniques and allow tracer input and retrieval of sediment after deployment. With these new devices, it is possible to measure accurately the variations of the solute concentrations with time.

By monitoring solute concentrations as a function of time, one can deduce the flux of these solutes out of or into the sediment using the relation:

$$V_{\text{ch}} \frac{dC_{\text{sol}}^{\text{ch}}}{dt} = S_{\text{ch}} F_{\text{sol}}^{\text{SWI}} \quad (2)$$

where V_{ch} and S_{ch} are respectively the volume and surface of the benthic chamber, and $C_{\text{sol}}^{\text{ch}}$ is the concentration of the solute in the chamber. This relation is valid at any time.

If the flux is constant during deployment (*i.e.* if the composition of the sediment remains unchanged for the course of the experiment), and if the chamber has a simple geometrical shape (*e.g.* cylindrical or rounded square), this relation can be integrated and rewritten:

$$C_{\text{sol}}^{\text{ch}} = \frac{F_{\text{sol}}^{\text{SWI}}}{H} t + C_{\text{sol}}^{\text{ch}} \Big|_{t=0} \quad (3)$$

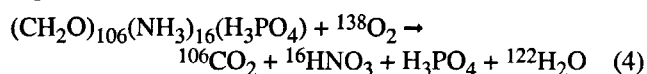
where H is the height of the benthic chamber and $C_{\text{sol}}^{\text{ch}} \Big|_{t=0}$ the initial concentration of the dissolved species in the benthic chamber. Hence, a linear regression of concentration in the benthic chamber versus time yields the flux of the solute through the sediment-water interface.

This paper addresses the interpretation of the data and calculation of fluxes obtained during benthic chamber deployments using numerical experiments. It focuses on the assumptions used in these interpretations, *e.g.* the constant composition of the sediment. The model has also been developed as a predictive tool in order to optimize the deployment of benthic chambers in the deep sea. Given a few parameters (POC flux, O_2 concentration in the bottom water, sedimentation rate, porosity) it simulates the whole course of an experiment and the subsequent variations of the sediment composition. It is consequently very useful in optimizing the deployments of a free vehicle during a cruise.

Modeling of the organic carbon transformation at the sea floor

The model used to describe the behavior of O_2 , organic carbon and phosphate during the deployment of a benthic chamber is an extension of the work presented by Rabouille and Gaillard (1991). The previous model was designed for calculating the distributions of organic carbon and oxygen at steady state. A detailed discussion of the parameterization of the processes affecting organic carbon and oxygen is given in Rabouille and Gaillard (1991). The following section only provides a short description.

The model expresses mathematically the different transport and biogeochemical processes affecting the distribution of dissolved oxygen and particulate organic carbon. In deep-sea sediments, organic matter is mineralized below the sediment-water interface by bacterial activity. The first centimetres of the sediment are generally oxic and, in this zone, bacteria utilize principally oxygen as terminal electron acceptor in their metabolism. This complex and multistep process can be represented using a net chemical reaction based on averaged stoichiometries of the particulate organic matter:



When oxygen is consumed together with organic matter, phosphate, nitrate and CO_2 are produced. The term phosphate stands for total concentration of dissolved phosphate (*i.e.* $[PO_4 = H_3PO_4 + H_2PO_4^- + HPO_4^{2-} + PO_4^{3-}]$) which is independent of the pH of the pore waters. The stoichiometry used in this paper is not totally realistic, especially for

the C/P ratio, which is very dependent on the sedimentary conditions (see discussion in Ingall and Van Cappellen, 1990), but it represents a case study. A different stoichiometry would not change the conclusions of this paper to any great extent. Phosphate is also subject to adsorption-desorption processes on mineral surfaces such as iron oxides. At steady state, this rapid exchange process does not alter the shape of the profile but it may introduce some buffering of the phosphate evolution in transient state (*i.e.* during the evolution of the benthic chamber model).

The sediment model relies on the differential mass balance equation proposed by Berner (1980). Transport is assumed to occur through molecular or ionic diffusion in porous medium for the dissolved species and through constant bioturbation and advective burial for Org-C. The kinetics of the bacterially-mediated oxidation of organic matter is represented by a modified Monod's rate law (see Tab. 1). This formulation couples the electron acceptor and the organic carbon in a kinetic expression for oxygen consumption and organic carbon mineralization. It accounts for the dependence of the mineralization rate on the metabolizable organic carbon concentration (Westrich and Berner, 1984) and on oxygen concentration below $3 \mu\text{mol/l}$ (Devol, 1975).

The boundary conditions of the steady-state model are a constant flux of organic carbon settling onto the sediment (F_c) and concentrations of oxygen and phosphate at the sediment-water interface equal to those of the overlying bottom water ($O_{2\text{BW}}$, $PO_{4\text{BW}}$).

This steady-state model serves to calculate the initial concentration profiles before the simulation of the benthic chamber deployment.

Description of the benthic chamber model

In order to describe the evolution of the sediment properties during the benthic chamber experiment, the steady-state model has been transformed into a transient model in which sedimentary distributions of solids and solutes are allowed to evolve with time (see equations in Table 1). In this regard, the value of some of the parameters must be altered in order to simulate the deployment of a benthic chamber. The flux of carbon (F_c) is canceled during the deployment, since the surface covered by the benthic chamber is isolated from its environment. Similarly, the accumulation of sediment ceases, since it results from the deposition of new particles at the interface. The activity of the fauna (meio- and macro-fauna) causing bioturbation is assumed to remain constant during deployment. This might be questionable because of the progressive depletion of oxygen in the sediment. The motile benthic fauna probably move out of the suboxic zone, but bioturbation is surely as intense (if not more) in the oxic zone as it was before the deployment. Therefore our assumption of constant bioturbation is not unrealistic. A new boundary condition at the sediment-water interface was introduced in order to describe the transient state. At this interface, the concentration of a solute varies according to the accumulation or depletion in the benthic chamber (Eq. 1.4). These changes are

Table 1

System of three equations representing organic carbon oxidation, oxygen consumption and phosphate production in a surficial sediment. For the calculation of steady state, the dC/dt were set to zero and a constant flux of organic carbon was imposed at the sediment-water interface. For transient states, this flux was set to zero together with the advection term (w).

Main equations:	
$D_s \frac{\partial^2 \text{Corg}}{\partial x^2} - \omega \frac{\partial \text{Corg}}{\partial x} - R_{\text{max}} \text{Corg} \frac{\text{Ox}}{\text{Ox} + K_m} = \frac{\partial \text{Corg}}{\partial t}$	(1.1)
$\phi D_s \frac{\partial^2 \text{Ox}}{\partial x^2} - (1 - \phi) \gamma_{\text{ox}} R_{\text{max}} \text{Corg} \frac{\text{Ox}}{\text{Ox} + K_m} = \phi \frac{\partial \text{Ox}}{\partial t}$	(1.2)
$\phi D_s \frac{\partial^2 \text{PO}_4}{\partial x^2} + (1 - \phi) \gamma_{\text{p}} R_{\text{max}} \text{Corg} \frac{\text{Ox}}{\text{Ox} + K_m} = \phi \frac{\partial \text{PO}_4}{\partial t}$	(1.3)
Boundary conditions:	
$\left. \frac{\partial C}{\partial t} \right _{x=0} = \frac{\phi D}{H} \left. \frac{\partial C}{\partial x} \right _{x=0}$	$C = \text{Ox or PO}_4$, (1.4)
$\frac{d\text{Corg}}{dx} = \frac{d\text{Ox}}{dx} = \frac{d\text{PO}_4}{dx} = 0$	For $x = \infty$ (1.5)

Corg: Particulate organic carbon content in the solid (nmol/cm³ of solids)

Ox: Oxygen concentration in the interstitial water (nmol/cm³ of liquid)

PO₄: Phosphate concentration in the interstitial water (nmol/cm³ of liquid)

D_B: Biological dispersion coefficient (3x10⁻⁹ cm²/s)

D_{ox}: Molecular diffusion coefficient for O₂ in the sediment (6.5 × 10⁻⁶ cm²/s)

D_{PO4}: Molecular diffusion coefficient for PO₄ in the sediment (2.2 × 10⁻⁶ cm²/s)

ω : Advection rate for the solids (5 × 10⁻¹¹ cm/s)

R_{max}: Maximum organic matter degradation rate (s⁻¹)

γ_{O_2} : Oxygen: carbon ratio for the decomposition of organic matter (138/106)

γ_{PO_4} : Phosphate: carbon ratio in decomposing organic matter (1/106)

K_m: Monod constant for oxygen utilization by bacteria (3.1 nmol/cm³)

ϕ : Porosity of the sediment (85 %)

F_c: Flux of particulate organic carbon towards the sediment (nmol cm⁻² s⁻¹)

x : depth in the sediment relative to the sediment-water interface counted positively downward (cm)

χ : maximum depth considered during the calculations (5 cm)

H: Height of the cylindrical benthic chamber (10 cm)

the result of uptake (w) or release from the sediment. This can be expressed as:

$$\left. \frac{\partial C_{\text{ch}}}{\partial t} = \frac{\phi D}{H} \frac{\partial C_{\text{sed}}}{\partial x} \right|_{\text{swi}} \quad (6)$$

where,

C_{ch}: Concentration of the solute in the benthic chamber

C_{sed}: Concentration of the solute in the sediment.

D: Diffusion coefficient of the solute

ϕ : Porosity

H: Height of the water column enclosed in the benthic chamber

SWI: Sediment-water interface.

The boundary condition at the sediment-water interface for the organic carbon is that the flux of particulate matter is set to zero when the chamber is set in place. To solve the set of equations presented in Table 1, six boundary conditions are required. The three remaining conditions are for the lower spatial boundary: we have assumed that at infinite depth no concentration changes occur. In our case, this infinite depth was chosen to be 5 cm for the three species (Eq. 1.5), because gradients spread down to a maximum of 4 cm.

The three time-dependent equations were discretized using a Crank-Nicholson scheme which minimizes the truncation error during the calculation (Carnahan *et al.*, 1969) and solved numerically. Transient mass balance calculations were performed in order to confirm the validity of the calculations. They were calculated as the difference between the stock variation with time and the flux through the interface plus the rate of mineralization. This difference has the unity of a flux and is at most two orders of magnitude lower than the flux through the sediment-water interface for the dissolved components (O₂ and PO₄).

We have also performed mass balance calculations on the whole system. The organic carbon inventory in the sediment shows a slight tendency to decrease more rapidly than its consumption rate would allow. However, this departure, produced as a result of rounding errors during calculations, does not exceed 10⁻⁴ % as calculated in the top three centimeters of the sediment. This accuracy is consequently satisfactory for such calculations.

Potential effect of the diffusive boundary layer

In the deep ocean, the water overlying the sediments is constantly subject to motion, while, the sediments are fixed on the sea floor, with the exception of sporadic resuspension events due to higher shear stress on the deposited particles. In consequence, a stagnant film of water is present at the sediment-water interface which results from the annihilation of the current speed at the contact of the solid interface. This stagnant film may interfere with the diffusive fluxes out of and into the sediment, since it offers a resistance to diffusion. The thickness of the diffusive boundary layer (DBL) has been estimated by different means, and ranges from 500 to 1200 μm on the deep-sea floor (Santschi *et al.*, 1983; Santschi *et al.*, 1991). The effect of the DBL on the net diffusive fluxes depends on the relative magnitude of the supply or removal by diffusion and the consumption or production rate (Boudreau and Guinasso, 1982; Santschi *et al.*, 1991). If the reaction in the sediment proceeds at a high rate, the transport through the DBL is the limiting step and the thickness of the diffusive layer becomes an important parameter in the control of solute fluxes.

If we assume that no oxygen consumption occurs in the diffusive sublayer, the diffusive flux through the interface

is equal to the diffusive flux through that layer. Because the chemical gradient of O_2 extends over a larger length scale than the conventional diffusive boundary layer thickness (*i.e.* the penetration depth of oxygen is 1 cm after 150 hours of deployment (Fig. 2b), and the DBL thickness is 1 mm maximum), the rate of transfer through the interface is governed by the combined rate of consumption and transport of O_2 in the sediments (Boudreau and Guinasso, 1982). This approximation is not valid when the chemical gradient of O_2 becomes expressed on a length scale equivalent to the DBL thickness, *i.e.* when the benthic chamber runs anoxic.

Our purpose here is to compare different alternatives for computing the actual sediment oxygen demand, *i.e.* shortly after deployment. It is hence not relevant to take the existence of the diffusive boundary layer into consideration in our calculation.

RESULTS

Two series of calculations have been performed using two different sets of parameters representative of sediments situated under mesotrophic or eutrophic surface oceanic water. In the first case, the flux of particulate organic carbon to the sea floor at steady state is set to a high value $F_c = 472 \text{ mmol C m}^{-2} \text{ yr}^{-1}$ (Case 1). The kinetic constant of the decomposition of organic carbon by oxygen is set

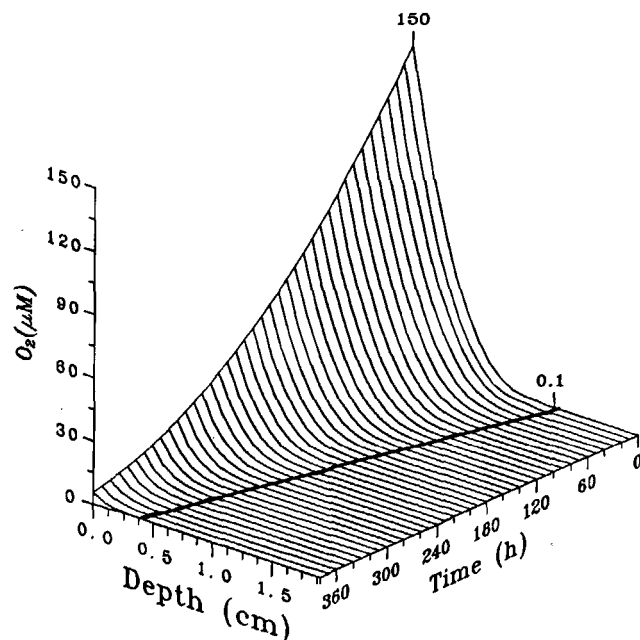


Figure 2a

Evolution of the concentration-depth profile of oxygen versus time in the high-flux case (case 1, $F_c = 472 \text{ } \mu\text{mol m}^{-2} \text{ yr}^{-1}$). The full line spotted with 0.1 represents the penetration depth of oxygen as a function of time.

Évolution du profil vertical de concentration de l'oxygène en fonction du temps dans le cas de flux de matière organique particulaire élevé (cas 1, $F_c = 472 \text{ } \mu\text{mol m}^{-2} \text{ yr}^{-1}$). La droite indiquée par 0.1 représente la pénétration de l'oxygène en fonction du temps.

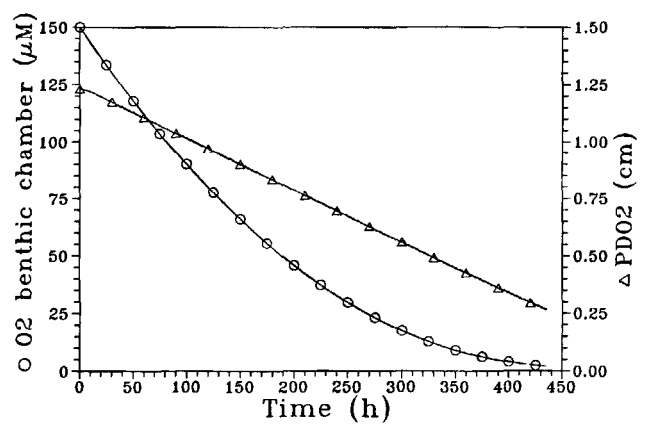


Figure 2b

Evolution with time of the concentration of oxygen in the benthic chamber and the penetration depth of oxygen (PDO_2) in the sediment for the high-flux case ($F_c = 472 \text{ mmol m}^{-2} \text{ yr}^{-1}$).

Évolution avec le temps de la concentration d'oxygène dans la chambre benthique et de la profondeur de pénétration de l'oxygène (PDO_2) dans les sédiments (cas 1, $F_c = 472 \text{ mmol m}^{-2} \text{ yr}^{-1}$).

equal to $R_{max} = 0.09 \text{ yr}^{-1}$, this value compares well to mean values for the deep continental slope. In another case, we present a more usual situation for the deep sea-floor. The organic carbon flux at steady state is assumed to be $F_c = 190 \text{ mmol C m}^{-2} \text{ yr}^{-1}$ (Case 2) and the kinetic constant is $R_{max} = 0.03 \text{ yr}^{-1}$.

In both cases, the concentration in the water overlying the sediment at the beginning of the simulation are: $O_{2BW} = 150 \text{ } \mu\text{mol/l}$, $PO_{4BW} = 1 \text{ } \mu\text{mol/l}$. The height of the water column in the benthic chamber is set equal to 10 cm. The bioturbation coefficient (D_B) was assumed to be $0.09 \text{ cm}^2/\text{yr}$, which represents a mean value for the deep-sea sediments. The porosity was set to 85 % and the burial rate at 1.5 cm/kyr .

Oxygen in the high-flux case (Case 1)

Figure 2a displays the evolution with time of the oxygen profile in the case of a high organic carbon flux (Case 1). Each line on the graph represents a concentration profile calculated at a time interval of 10 hours. The evolution of the concentration profiles is reported for a simulation time of 380 hours (16 days). At this time, the oxygen concentration in the chamber reaches $5 \text{ } \mu\text{M}$. We have arbitrarily defined the penetration depth of oxygen (PDO_2) as the depth at which O_2 is equal to $0.1 \text{ } \mu\text{M}$. The evolution of the PDO_2 is displayed on the graph by the line labeled by 0.1. It is interesting to note that the whole profile undergoes an evolution. Most of the profile changes are achieved through diffusion which is an effective way to transport dissolved species on small distances (a few centimetres). However, due to lower gradients at depth, the solutes diffuse more slowly in deeper parts of the sediment. This is seen on Figure 2b, where the oxygen concentration at the interface decreases more rapidly than the penetration depth of oxygen. Hence, the gradient at the interface tends to be smoothed down with time and the flux changes during the course of the deployment.

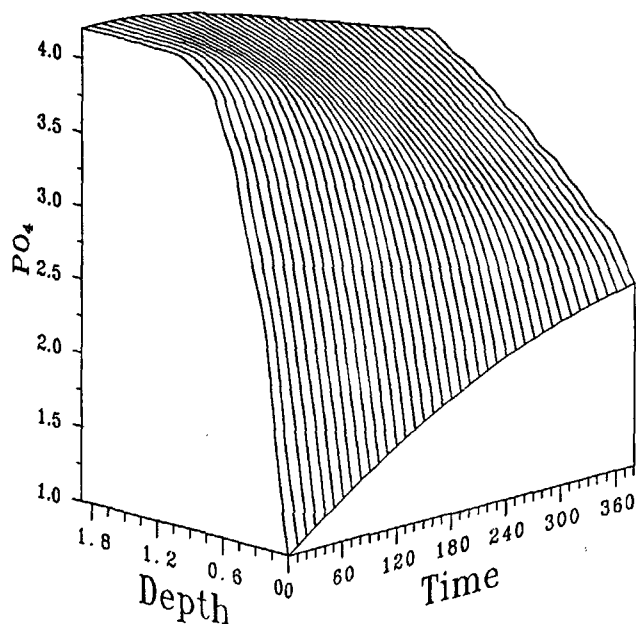


Figure 3a

Phosphate concentration profile evolution with time in the high-flux case ($F_c = 472 \text{ mmol m}^{-2} \text{ yr}^{-1}$).

Evolution au cours du temps du profil vertical de phosphate dissous dans le cas 1 ($F_c = 472 \text{ mmol m}^{-2} \text{ yr}^{-1}$).

Phosphate in the high-flux case (Case 1)

The evolution of the phosphate profiles is shown in Figure 3a. Two processes strongly influence the changes with time of the phosphate profile. The accumulation of dissolved phosphorus in the benthic chamber lowers the flux of dissolved phosphate out of the sediment. In addition, the production of dissolved phosphate from the mineralization of organic matter decreases due to the depletion of oxygen. Hence, the general trend is, as with oxygen, to reduce the gradients. The concentration at 2 cm depth decreases slightly (from 4.2 to 3.6) while the concentration

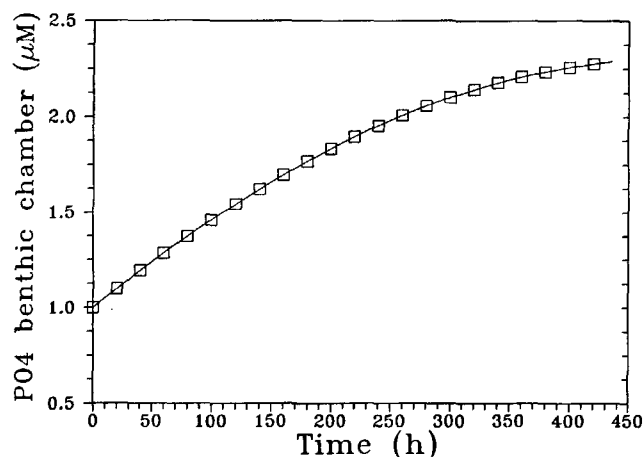


Figure 3b

Concentration of phosphate in the benthic chamber as a function of time.

Concentration de phosphate dissous dans la chambre benthique en fonction du temps (cas 1, $F_c = 472 \text{ mmol m}^{-2} \text{ yr}^{-1}$).

at the sediment-water interface is doubled. The variation with time of the concentration of ΣPO_4 in the benthic chamber is presented on Figure 3b. This plot exhibits a curvature similar (but inverse) to that of oxygen shown on Figure 2b. In this model, phosphate production is closely, and solely, dependent on oxygen reduction, since these two species are related through the stoichiometric decomposition of organic matter (Eq. 4). However, the geochemical behavior of ΣPO_4 during early diagenesis in marine sediments is complicated by adsorption/desorption reactions at the solid/water interface. The accumulation of dissolved phosphate in the sediment and hence the reduction of the flux out of the sediment would probably be slowed by the buffering adsorption of phosphate on mineral particles.

In this calculation, adsorption-desorption processes were not taken into account. Hence, the results of the calculations performed here are given as a case study of a nutrient produced by the mineralization of particulate organic matter. The evolution with time for a benthic chamber experiment would be similar for nitrate in completely oxic sediments or ΣCO_2 in sediment above the carbonate compensation depth (CCD).

It is important to note that the concentration of phosphate in the chamber varies from $1 \mu\text{M}$ to $2 \mu\text{M}$ in the first stage of the experiment. This variation is small and should be relatively difficult to determine during an *in situ* experiment due to the analytical error in phosphate determination at the micromolar level and problems related to sampling and the recovery procedure. In sediments of this type, and because of the chemical properties of phosphate in sedi-

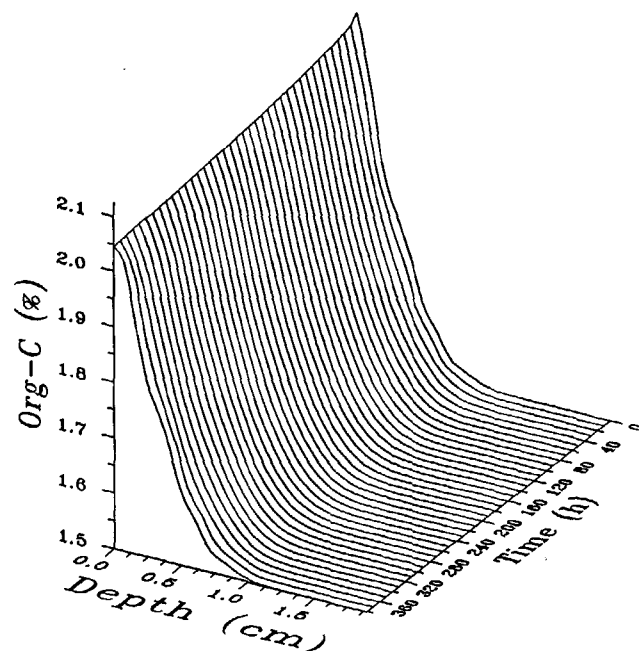


Figure 4

Plot showing the metabolizable organic carbon concentration in percent of the dry solid as a function of depth and time in the high-flux case.

Diagramme représentant la concentration de carbone organique métabolisable en pourcent du poids de solide sec en fonction du temps et de la profondeur dans le cas d'un flux élevé.

ments mentioned above, it is very difficult to determine the flux of ΣPO_4 through the sediment-water interface. Not surprisingly then, benthic ΣPO_4 fluxes in the deep open ocean have not yet been determined with confidence.

Particulate organic carbon in the high-flux case (Case 1)

The concentration profiles of organic carbon (Fig. 4) do not exhibit important changes throughout the entire simulation. The concentration at the sediment-water interface varies from 2.1 % to 2.05 % of the dry solid and the concentration at 2cm depth remains unchanged over the time course of the simulation.

Low-flux case (Case 2)

The description given in the high-flux case holds for the low-flux case. This concerns the flattening of the gradient at the sediment-water interface for the solutes and the relative conservative behavior of the particulate organic car-

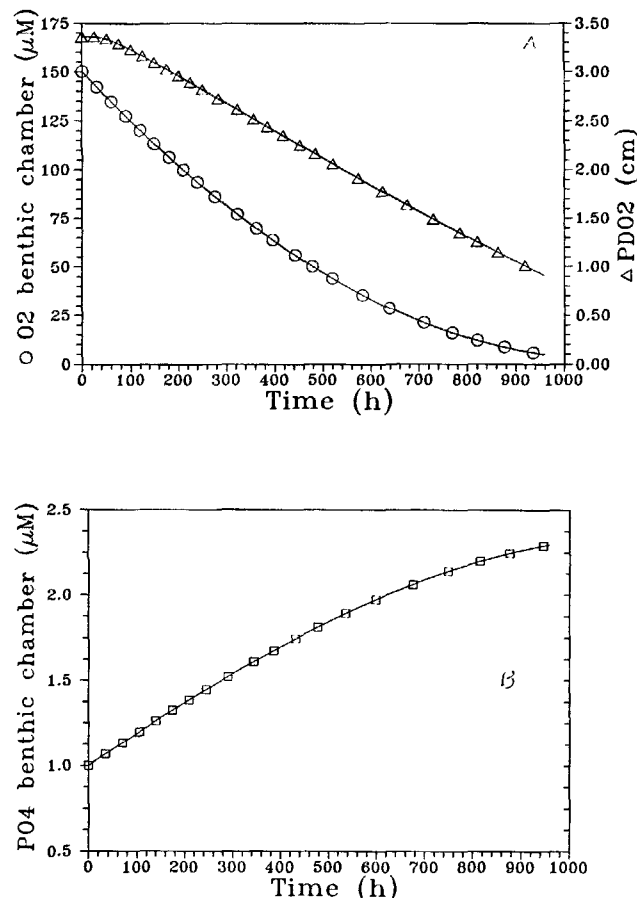


Figure 5
 General plot for the low flux case (Case 2, $F_c = 190 \text{ mmol m}^{-2} \text{ yr}^{-1}$). (a) Oxygen concentration in the chamber and PDO_2 in the sediment variations with time. (b) Phosphate in the chamber as a function of time. At 955h, oxygen reaches the $5 \mu\text{M}$ level.

Diagramme général pour le cas d'un flux de carbone organique particulaire peu élevé (Cas 2, $F_c = 190 \text{ mmol m}^{-2} \text{ yr}^{-1}$). (a) Concentration d'oxygène dans la chambre benthique et PDO_2 dans le sédiment. (b) Concentration de phosphate dans la chambre benthique en fonction du temps. A 955 heures, l'oxygène atteint le niveau de $5 \mu\text{M}$.

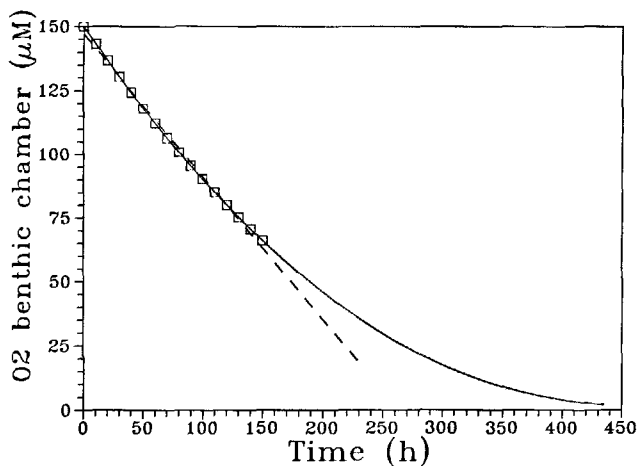


Figure 6
 Test of the linear model. The dashed line represents the linear best fit. Squares are sampled at 10-hour intervals using the simulated data set and the full line represents the model evolution curve.

Test du modèle linéaire. La ligne pointillée représente le meilleur ajustement linéaire. Les carrés sont « échantillonnés » à 10 heures d'intervalle dans nos données simulées et la ligne pleine représente la courbe d'évolution du modèle.

bon. The situation in this low-flux case differs from the high-flux case because the oxygen demand at steady state is lower. For this reason, the time for oxygen to reach the $5 \mu\text{M}$ level in this case (955 hours) is largely increased in comparison with the previous case.

The low-flux case ($190 \text{ mmol C m}^{-2} \text{ yr}^{-1}$) corresponds to a sediment that would be situated in a mesotrophic oceanic region. We present in Figure 5 the variations as a function of time of the concentration of oxygen and phosphate in the benthic chamber as well as the evolution of the penetration depth of oxygen in the sediment calculated during the simulation.

In the next two sections, we will focus on oxygen behavior, because of its importance as an electron acceptor in the sediments.

Testing the validity of the linear approximation

The simplest means of calculating solute fluxes with benthic chamber experiments is the linear regression (Elderfield *et al.*, 1981; Devol, 1987 and others). The hypothesis introduced by this technique is that gradients which support the transfer of dissolved matter to or from the chamber are not altered during deployment. If the deployment time is short and the change of concentration in the chamber low enough, one can assume the solute fluxes to be constant.

We have performed this regression technique using the oxygen values from the high-flux case simulation. We sampled simulated O_2 concentration values at 10-hour intervals during the first 150 hours. This time period corresponds to a decrease of $\approx 50 \%$ of the initial O_2 concentration in the chamber for the first case (high-flux). Figure 6 displays the comparison between the regression

analysis performed and the original data set. On this graph, the squares represent the simulated points, the full line represents our model-computed evolution, and the dashed line represents the best linear fit obtained for the first 150 hours. The flux calculated by the linear regression is $488 \text{ mmol O}_2 \text{ m}^{-2} \text{ yr}^{-1}$ while the sedimentary oxygen demand at steady state is $606 \text{ mmol O}_2 \text{ m}^{-2} \text{ yr}^{-1}$. This result indicates that, for a long term deployment, the bias introduced by the linear regression technique alone is around 20 % on the oxygen flux to the sediment. It must be pointed out that this offset is a consequence of the mathematical treatment (linear hypothesis) and that the uncertainty related to contamination, a to experimental or analytical problems, would add to it.

To reduce the effect of non-linearity of the curve of oxygen versus time, Smith *et al.* (1983) have proposed consideration of only those the oxygen concentrations that were in excess of 75 % of the initial value. This represents a simulated deployment time of 60 hours, more compatible with real experiments. With this approach, the calculation error is reduced to 10 % in the calculation mentioned above. As shown by Bender *et al.* (1989), and as may be intuited, this interpretation error is a direct function of the volume of the overlying water enclosed and the magnitude of the sediment oxygen demand. In other words, if the volume of water enclosed in the chamber becomes smaller, the oxygen concentration in the chamber decreases more rapidly. Therefore, this produces an evolution of oxygen concentration versus time that deviates more rapidly from the linear approximation.

Comparison with non steady-state models

Two models describing the oxygen behavior in the sediment and the benthic chamber during a deployment have been recently introduced (Bender *et al.*, 1989; Hall *et al.*, 1989). These models show some similarities but differ in the calculation approach. They both describe the transport through molecular diffusion and the reaction affecting oxygen in the sediment by a zero-order kinetic. This zero-order kinetic is supported by the relative constancy of organic carbon on the spatial scale of investigation (<1 cm) and by the independence with respect to the oxygen concentration of the aerobic respiration at values greater than $5 \mu\text{M}$. The equation describing the system is:

$$D_{\text{O}_2} \frac{\partial^2 \text{O}_2}{\partial x^2} - A = \frac{\partial \text{O}_2}{\partial t} \quad (7)$$

D_{O_2} : Diffusion coefficient of O_2 in sediment pore water

O_2 : Oxygen concentration in the pore water

x : Depth in the sediment

t : Time

A : Reaction term constant with depth (zero order)

Hall *et al.* (1989) considered in their mathematical derivation that the concentration profile of oxygen remains close to steady state at each time step (*i.e.*, $\partial \text{O}_2 / \partial t = 0$), whereas Bender *et al.* (1989) have used a numerical scheme to compute the transient solutions of equation (7) with appropriate

boundary conditions. In the following, we briefly derive the basic equations used by Hall *et al.* (1989) since their model has an analytical solution, which will serve for comparison with our results. The steady-state approximation of equation (7) is integrated with the following boundary conditions:

(i) the concentration of O_2 at the sediment-water interface is equal to the concentration in the overlying water (O_2^{bw}),

(ii) oxygen reaches zero at the penetration depth of oxygen (PDO₂).

This is expressed mathematically by the following expressions:

$$(i) \quad x = 0 \quad \text{O}_2 = \text{O}_2^{\text{bw}}$$

$$(ii) \quad x = \text{PDO}_2 \quad \text{O}_2 = 0$$

The solution for the distribution of the concentration of oxygen with depth is therefore:

$$\text{O}_2 = (A / 2D_{\text{O}_2})x^2 - \sqrt{2\text{O}_2^{\text{bw}} A / D_{\text{O}_2}} x + \text{O}_2^{\text{bw}} \quad (8)$$

and the flux at the sediment-water interface is:

$$F_{\text{O}_2}^{\text{swi}} = \sqrt{2\text{O}_2^{\text{bw}} A D_{\text{O}_2}} \quad (9)$$

By inserting the flux parameterization of eq. (9) in equation (2), and integrating the equation because O is also the oxygen concentration in the chamber (O), the evolution is given by

$$\text{O}_2^{\text{BC}} = \left[\sqrt{\text{O}_{2\text{in}}^{\text{BC}}} - \sqrt{A D_{\text{O}_2} / 2h^2 t} \right]^2 \quad (10)$$

where $\text{O}_{2\text{in}}^{\text{BC}}$ is the initial O_2 concentration in the benthic chamber and h the height of the water column in the benthic chamber.

One of the assumptions of this model is that at each time step steady state is re-established. Following Hall *et al.*,

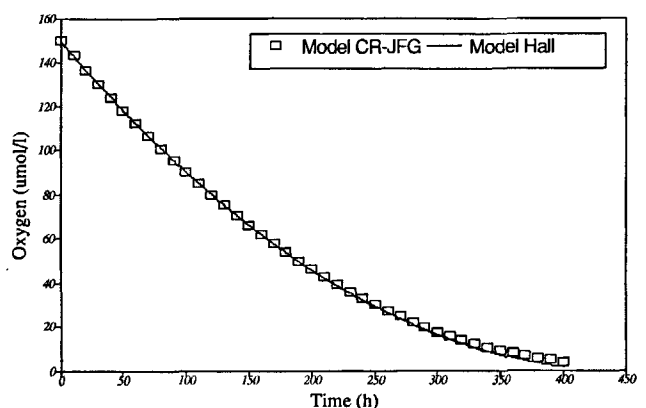


Figure 7

Variation of oxygen concentration in a benthic chamber. The squares represent the model of this paper (CR-JFG) used as data for the fit of the model of Hall *et al.* (1989) (solid line). The flux of organic carbon at steady state is $F_c = 472 \text{ mmol C m}^{-2} \text{ yr}^{-1}$

Variation de la concentration d'oxygène dans la chambre benthique. Les carrés représentent le modèle décrit dans cet article (CR-JFG) utilisé comme données pour l'ajustement du modèle de Hall *et al.* (1989) (ligne pleine). Le flux de carbone organique à l'état stationnaire de départ est $F_c = 472 \text{ mmol C m}^{-2} \text{ yr}^{-1}$.

(1989), this assumption is valid for oxygen if the depletion time in the chamber (T_w , time to drive the oxygen concentration to zero in the chamber) is far greater than the re-equilibration time in the sediment (T_s). The ratio T_s/T_w is approximated by the ratio $2*PDO_2/h$ (Hall *et al.*, 1989). In the cases described in this paper this ratio is equal to 0.24, which is probably at the limit of validity of the steady-state approximation.

In order to compare the results obtained with this simpler calculation and our approach, a benthic chamber experiment has been simulated. The variations of the concentration of O_2 in the benthic chamber obtained by our model are presented in Figure 7 (squares). These values have then been treated as an input data set and fitted using the model of Hall *et al.* This fit allowed us to compare the initial oxygen demand recalculated with the model of Hall *et al.* (1989) to the initial value assigned in the steady-state model. The fit is done on the first 100 hours which is a very common deployment time for deep-sea sediments. The agreement between the two values of the initial flux (Tab. 2) is much better than for the linear fitting technique (around 2 to 5 %). It demonstrates that the model developed by Hall *et al.*, (1989) has for more practical cases a sufficient quality to interpret field data.

The agreement between the concentration of oxygen expressed as a function of time obtained using our model and that of Hall *et al.* (1989) is fair during the first part of the deployment (250 hours). But a net shift is observed afterwards (Fig. 7), when the oxygen value is below 30 $\mu\text{mol/l}$. This demonstrates the inability of the simple zero-order model to describe long term incubations because the kinetic formulation does not consider its dependence on the organic carbon concentration and oxygen at low concentrations.

One basic assumption of the models of Hall *et al.* (1989) and Bender *et al.* (1989) is the zero-order kinetic. This type of kinetic formulation implies that the Overall Rate of Oxygen Consumption (OROC) is proportional to the Penetration Depth of Oxygen (PDO).

$$OROC = \int R dx = \int_{x=0}^{x=PDO_2} A dx = A PDO_2 \quad (11)$$

This assumption can be tested with our model since it provides a more realistic handling of the kinetic expression. The results displayed on Figure 8 show a linear decrease of the penetration depth of oxygen and the OROC until 350h.

Table 2

Comparison of the initial oxygen demand at the sediment-water interface (in $\text{mmol } O_2 \text{ m}^{-2} \text{ yr}^{-1}$) between the two models and in the two cases corresponding to different organic carbon fluxes at steady state. Low: $F_c = 190 \text{ mmol } C \text{ m}^{-2} \text{ yr}^{-1}$ and High: $F_c = 472 \text{ mmol } C \text{ m}^{-2} \text{ yr}^{-1}$.

	This model assigned initial O_2 flux	Hall's Model initial O_2 flux	Difference (%)
Low	242	230	5
High	605	589	3

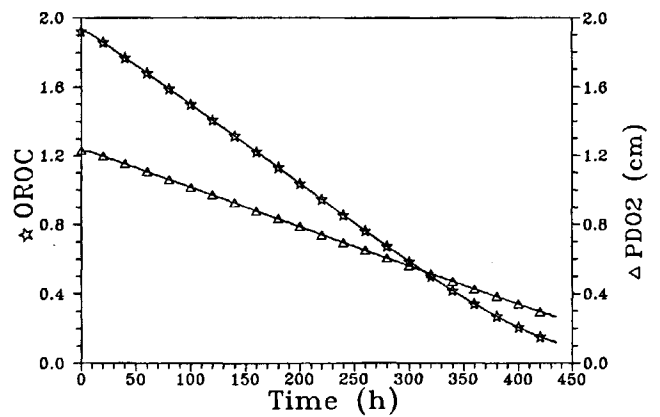


Figure 8

Overall rate of O_2 consumption of the sediment (OROC in $10^{-3} \text{ mmol } O_2 \text{ cm}^{-2} \text{ s}^{-1}$) plotted versus time. A 20-fold decrease over the period of the simulation is shown. The penetration depth of oxygen (PDO_2), also plotted for comparison, decreases by a factor of five.

Le taux de consommation de O_2 par les sédiments (OROC en $10^{-3} \text{ mmol } O_2 \text{ cm}^{-2} \text{ s}^{-1}$) est représenté en fonction du temps. Il montre une décroissance d'un facteur 20 sur la durée de la simulation. La pénétration de l'oxygène (PDO_2) est aussi représentée pour comparaison. Elle décroît d'un facteur cinq.

In the model of Hall *et al.* (1989), the decrease of PDO_2 and OROC is linear. As a matter of fact, we have:

$$PDO_2 = \sqrt{20_2^{bw} D_{O_2} / A} \quad (12)$$

When combined with equation 10, we obtain:

$$PDO_2 = PDO_2^m - \frac{D}{h} t \quad (13)$$

and

$$OROC = OROC_{in} - \frac{DA}{h} t \quad (14)$$

The subscript or superscript in indicates initial values (*i.e.* at $t = 0$).

The parameter D/h calculated with the parameters of our model is $2.34 \cdot 10^{-3} \text{ cm/h}$ ($D = 6.5 \cdot 10^{-6} \text{ cm}^2/\text{s}$ and $h = 10 \text{ cm}$). The value of the slope representing the variations PDO_2 versus time is $2.21 \cdot 10^{-3} \text{ cm/h}$ (Fig. 8). The agreement is fair and indicates that the zero-order model displays an evolution very close to the more complete model presented in this paper, as long as the concentration of oxygen is not too small.

CONCLUSION

In this paper, we have presented a model that calculates the changes of sediment and interstitial water composition during a benthic chamber experiment on the deep-sea floor. We have shown that the sediment pore water compo-

sition undergoes important changes during incubation while the solid phase remains virtually unaffected. The penetration depth of oxygen is greatly reduced. Consequently, this might introduce an important source of uncertainty if one estimates the flux of redox sensitive elements (cobalt, manganese, iron; Sundby *et al.*, 1986), when the chamber runs rapidly anoxic. These elements will be remobilized near the sediment-water interface and their flux could be artificially enhanced by the rapid depletion of oxygen from the sediment.

The calculations indicate that a direct estimation of the flux using concentration variation in the benthic chamber (linear model) may introduce a bias ranging from 10 to 20 % of the measured flux. Concurrently, the analytical zero-order model may represent a powerful alternative because it departs only by a few percentage points from the real initial flux of oxygen.

The model presented in this paper illustrates some of the processes that arise in the sediment during the oxidation of the organic matter by bacterial populations using oxygen. It has been proposed recently (Reimers, 1989) that most of the organic carbon mineralization occurs at the sediment water interface before significant burial.

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It would be interesting to test this hypothesis by comparing benthic flux measurements to the kind of model developed in this paper for a single site where organic carbon and oxygen micro-profiles are known. Thus the disparity between the model predictions and the flux data could serve to estimate the extent of benthic mineralization at the sediment-water interface.

The oxygen demand is ultimately linked to the rate of organic matter mineralization, and the precise quantification of this latter process is required for the determination of the sediment role in the global oceanic carbon cycle.

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