

## STUDY OF THE OXYGEN CONSUMPTION PROBLEMS INTO THE BENTHIC SEDIMENTS OF THE ACCUMULATION LAKES

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*Degradarea materiei organice depozitate duce la un flux de componente dizolvate ce pot afecta sever funcționarea biogeochimică și ecologică a coloanei de apă. Pe lângă eliberarea substanțelor dizolvate, sedimentele pot acționa ca o chiuvetă pentru nutrienți sau urmărirea metalelor rămase în sediment după depozitare, ducând la degradarea calității apei de suprafață și a ecosistemelor. Problema transportului de oxigen nu poate fi rezolvată direct prin combinarea ecuațiilor de transfer de masă și de mișcare hidrodinamică, deci ca soluții ale acestei probleme sunt propuse metode analitice-experimentale.*

*Degradation of the deposited organic matter drives a return flux of dissolved components, which may profoundly affect the biogeochemical and ecological functioning of the water column. In addition to releasing solutes, sediments may also act as a sink with nutrients or trace metals remaining in the sediment after deposition, posing a huge risk to surface water quality and ecosystems. The problem of oxygen transport can not be directly solved by combining the mass transfer and the hydrodynamic movement equations, so the closures of analytical-experimental nature are proposed as a solution to this problem.*

**Key words:** sediments, oxygen fluxes

### 1. Introduction

Each water use, including abstraction of water and discharge of wastes, leads to specific, and generally rather predictable, impacts on the quality of the aquatic environment. In addition to these international water uses, there are several human activities which have indirect and undesirable, if not devastating, effects on the aquatic environment. Examples are uncontrolled land use for urbanization or deforestation, accidental (or unauthorized) release of chemical substances; discharge of untreated wastes or leaching of noxious liquids from solid waste deposits. Similarly, the uncontrolled and excessive use of fertilizers and pesticides has long-term effects on ground and surface water resources.

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Accumulation lakes from hydropower plants are susceptible to eutrophication due to increased input of nutrients, nitrogen and phosphorus, from anthropogenic sources. Excess availability of nutrients stimulates primary production but can also have significant effects on microbial processes. Elevated primary production increases the amount of organic matter and thus increases the mineralization. The increased mineralization consumes oxygen ( $O_2$ ) in the hypolimnion, leading to anaerobic conditions in lake during stratification periods, favoring anaerobic microbial processes. In addition, nutrients can also affect bacterial metabolism and degradation pathways. Organic matter is predominantly degraded through microbial processes, which provide maximum energy yield [1]. Thermodynamic energy yield from the oxidation reactions with various electron acceptors decreases in the order of  $O_2$ ,  $NO_3^-$ ,  $Mn^{4+}$ ,  $Fe^{3+}$ ,  $SO_4^{2-}$  and  $CO_2$ . For example, when nitrate is abundant organic carbon is degraded through nitrate reduction in denitrification than through methanogenesis, which is a common mode of carbon degradation in non polluted freshwater sediments. Changes in degradation rates and pathways induced by eutrophication have atmospheric importance, since microbial processes produce important greenhouse gases carbon dioxide ( $CO_2$ ), methane ( $CH_4$ ) and nitrous oxide ( $N_2O$ ).

In freshwaters,  $CH_4$  is produced in anoxic sediments via methanogenesis and aerobically oxidized by methanotrophic bacteria if  $O_2$  is available in the sediment–water interface or water column. Thus, the  $O_2$  depletion can stimulate  $CH_4$  production in eutrophic lakes during stratifications and decrease  $CH_4$  oxidation leading to an increase in the emissions of  $CH_4$  from waters to the atmosphere.

Ammonium, which resembles chemical structure of the  $CH_4$  molecule, can interfere with the oxidation of  $CH_4$  because  $NH_4^+$  competes with  $CH_4$  for the methane mono-oxygenase, the key enzyme in  $CH_4$  oxidation. On the other hand,  $CH_4$  and  $NH_4^+$  oxidizing bacteria compete for  $O_2$ . In non-water saturated soils, where  $CH_4$  oxidation takes place at low  $CH_4$  concentrations, increased  $NH_4^+$  availability decreases the  $CH_4$  oxidation. In water saturated wetland soils and sediments, where the  $CH_4$  concentration is high and availability of  $O_2$  is low, the effects of  $NH_4^+$  on  $CH_4$  oxidation appear to be contradictory, with reports ranging from inhibition to stimulation. Nitrous oxide is produced from nitrification, in the oxidation of  $NH_4^+$  to nitrite ( $NO_2^-$ ), or from denitrification as an intermediate in the reduction of nitrate ( $NO_3^-$ ) to molecular nitrogen ( $N_2$ ). Ammonium and  $O_2$ ,

key substrates of nitrification, are therefore essential for  $N_2O$  production if no external  $NO_3^-$  is available.

In eutrophic freshwaters, where hypolimnion and sediment surface are often lacking in  $O_2$ , the availability of  $O_2$  regulates nitrification. Low nitrification activity further restricts denitrification, which often depends on  $NO_3^-$  produced from nitrification. Thus, the depletion of  $O_2$  reduces  $N_2O$  production in freshwater sediments. However, with a good  $O_2$  supply, the low availability of  $NH_4^+$  may limit nitrification and  $NO_2$  production in sediments. Nitrogen loading of freshwaters can significantly increase  $N_2O$  emissions. Ammonium and  $O_2$  do affect carbon and nitrogen transformation processes, but their additive effects on  $CH_4$  and  $N_2O$  release from lake sediments are uncertain [2].

## 2. The numerical model

The problem of an active solute diffusion from the water column into the sediment can be well described through a differential equation such as:

$$\frac{\partial C}{\partial t} = \frac{1}{\phi(z)} \frac{\partial}{\partial z} \left( D_{eff}(z) \frac{\partial C}{\partial z} \right) + R(z) \quad (1)$$

$$D_{eff}(z) = \frac{\phi(z)}{g^2(z)} D_{mol} + D_{turb}(z) + D_{disp}(z) \quad (2)$$

Where  $D_{eff}(z)$  is usually expressed in  $[cm^2s^{-1}]$ .

It is important to specify that the characteristics of the sediment (porosity and tortuosity), the diffusive coefficients and the consumption term strongly depend on the vertical coordinate ( $z$ ). For this proposed model, the porosity and tortuosity parameters assume the unitary value above the sediment-water interface and the consumption term is considered zero under and above the respective interface. The presence of the consumption term  $R(z)$  (dependent on the oxygen concentration) is described by a strongly non-linear equation, compromising the possibility to solve this problem using an analytical method.

To resume, the numerical model proposed [3] can be reduced to the following equations system:

$$\frac{\partial C}{\partial t} = \frac{1}{\phi(z)} \frac{\partial J(z)}{\partial z} + R(z) \quad (3)$$

$$J(z) = D_{eff}(z) \frac{\partial C}{\partial z}$$

and the proposed closure equations and the relative values of the characteristic parameters are presented in tables 1 and 2.

Table 1

### Closure Equations For The Numerical Simulation

$D_{eff}(z) = \frac{\phi(z)}{g^2(z)} D_{mol} + D_{turb}(z) + D_{disp}(z)$	(4)
$\phi(z) = \begin{cases} (\phi(0) - \phi(\infty)) \cdot \exp\left(\frac{z}{\alpha}\right) + \phi(\infty) & z \geq 0 \\ 1 & z < 0 \end{cases}$	(5)
$g^2(z) = a \phi(z)^{1-m}$	(6)
$D_{mol} = D_{mol}(T) = 10^{\left[-4.41 + 773.8/T - (506.4/T)^2\right]}$	(7)
$D_{turb}(z) = \begin{cases} \frac{1}{Sc_{turb}} \left[ kzu_* - 11k\nu \tanh\left(\frac{zu_*}{11\nu}\right) \right] & z \geq 0 \\ 0 & z < 0 \end{cases}$	(8)
$D_{disp} = 0.1 \cdot u_* \cdot a_{disp} \cdot d_p \cdot \begin{cases} 1 & z \geq 0 \\ e^{z/l_{disp}} & z \leq 0 \end{cases}$	(9)
$R(z) = \begin{cases} 0 & z \geq 0 \\ -\frac{K_{max} \cdot c(z)}{K_{mm} + c(z)} \cdot \left(1 - \exp\left(\frac{z}{l_R}\right)\right) & z < 0 \end{cases}$	(10)

Table 2

### Characteristic Parameters Of The Numerical Simulation

$\phi_0$	$0.8 \div 1$	-
$\phi_\infty$	0.38	-
$\alpha$	0.001	[m]
$a$	1.02	-
$m$	1.81	-
$Sc_{turb}$	0.86	-

$a_{disp}$	$0.02 \div 0.1$	-
$d_p$	$(2.5 \div 5) \cdot 10^{-4}$	[m]
$l_{disp}$	$(0.025 \div 2.5) \cdot 10^{-3}$	[m]
$K_{max}$	$3.2 \cdot 10^{-3} \div 1.28 \cdot 10^{-1}$	[ $mg\ l^{-1}\ s^{-1}$ ]
$K_{mm}$	$3.2 \cdot 10^{-5} \div 3.2 \cdot 10^{-1}$	[ $mg\ l^{-1}$ ]
$l_R$	$(0.025 \div 2.5) \cdot 10^{-3}$	[m]

For the stationary analysis were chosen as limits the concentration values for the extremes of the integration domains:  $C=0$  in the sediment (where it is assumed that the oxygen is completely consumed) and  $C=C_{bulk}$  in the water column (where the concentration value for oxygen does not depend on the consumption at the bottom of the sediment layer). In conceiving this model were taken into account the parameters that describe the physical properties of the solid matrix of the sediment, those that regard the consumption phenomena but also those specific for the diffusion. In a first stage it will be analyzed which one of these parameters have a major influence in the calculus of the oxygen fluxes at the interface,  $J$ , and on the depth of oxygen penetration,  $\delta_{ox}$ , key parameter for the structure and distribution of the benthic communities inside the sediment but also for the delimitation of the diagenetic oxido-reduction reactions [2].

### 3. Model's solution and sensibility analysis in stationary conditions

To simplify the sensibility analysis of the different parameters that influence the model's results it is assumed the stationary hypothesis ( $\partial/\partial t = 0$ ) with the purpose to individualize the parameters that govern this model, that have a real influence on the oxygen concentration profiles. The figure 1 distinguishes how the oxygen concentration profile calculated with the model, inside the Brinkman layer [4], has a translation towards the bottom with respect to the model that consider negligible the dispersive phenomena ( $D_{disp}=0$ ) and converges to the same values where  $D_{disp} \ll D_{turb}$ .

In the figures 2, 3 and 4 are represented different oxygen concentration profiles obtained by varying the main parameters of the model (the variation is limited at the value range suggested in literature). Seems that the porosity is not of major influence with respect to the depth of the oxidized layer and the concentration profiles gradients at the interface. The  $K_{mm}$  parameter appears to be influent for the depth of the oxidized layer only for values comparable with the

real concentration but nevertheless has to be mentioned that it had not a great influence in fluxes estimation. The sensibility of the parameters  $K_{max}$ ,  $adisp$ ,  $ldisp$ ,  $u^*$  is very important for the concentration profiles geometry (more on  $\delta_{ox}$  than on  $J$ ).

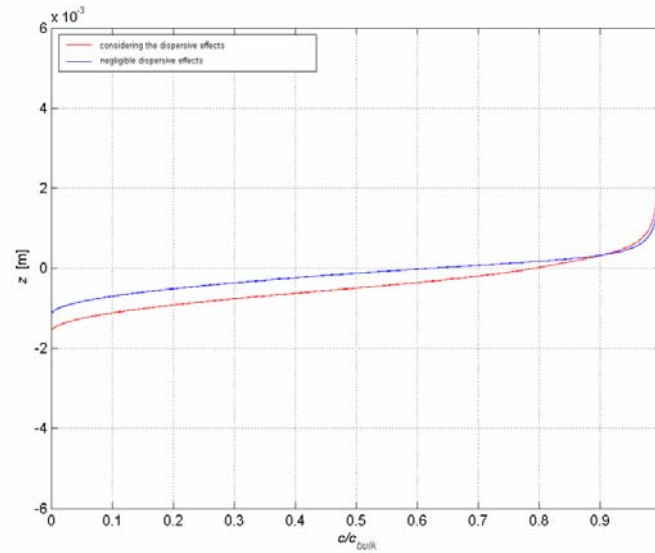


Fig 1 The influence of the dispersive effects on the oxygen concentration profiles

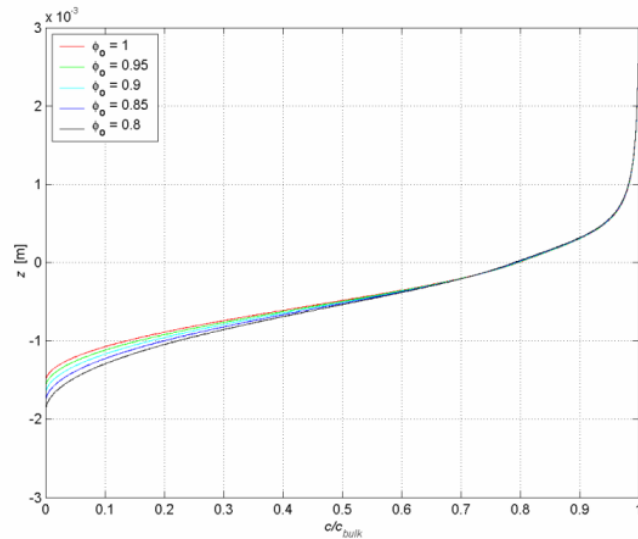
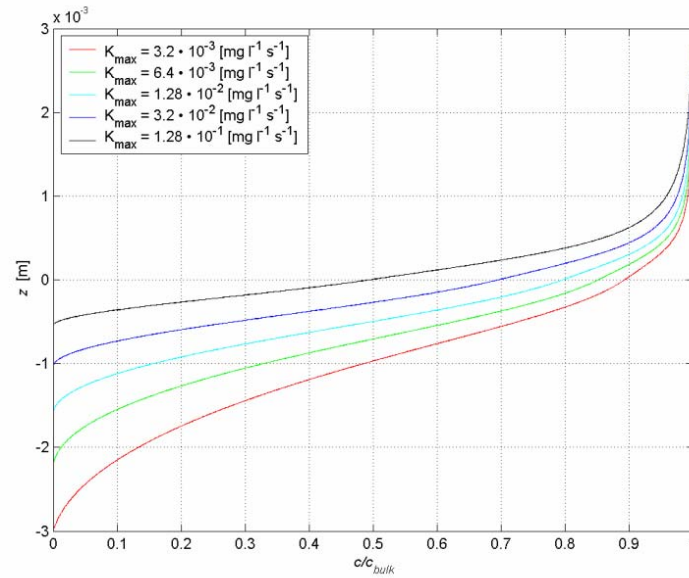
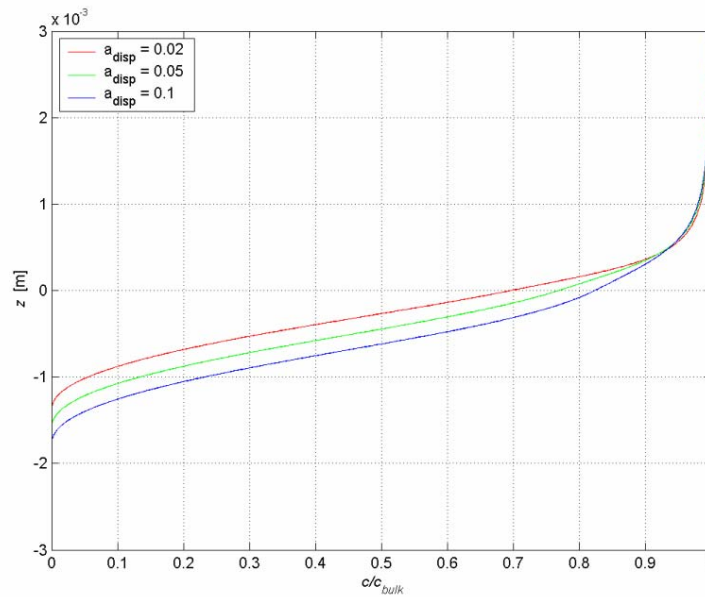


Fig 2 Sensibility analysis of the porosity on the concentration profile

Fig 3 Sensibility analysis of the parameter  $K_{\max}$  on the concentration profileFig 4 Sensibility analysis for  $a_{\text{disp}}$  parameter

Figures 5, 6 and 7 distinguish very well that the attrition velocity is a fundamental parameter of this model for the fluxes estimation (the dispersion

coefficients depend on it). The variation of  $u_*$  can lead to an increase (or decrease) of the fluxes at the interface of almost 6 times (see fig. 7). The fluxes increase is not proportional with  $u_*$  but seems asymptotic to a limit value  $\hat{u}_*$ .

A sensibility analysis, with respect to  $J$ , was performed for the characteristic parameters of the dispersion and turbulence phenomena with the variation of the attrition velocity. The variation of the sediment particles mean diameter ( $d_p$ ) and of the  $a_{disp}$  (fig. 5 and fig. 6) does not result significantly as it regards the flux (depending on the attrition velocity). The parameter  $l_{disp}$  (indirectly the depth of the Brinkman layer) seems fundamental for the correct estimation of  $J$  (see fig. 7). Particularly  $l_{disp}$  seems to be not very influent to the model's solution for low values of the attrition velocity. On the other hand,  $l_{disp}$  results to be the one that governs the limit value of  $\hat{u}_*$  for which the flux reaches an asymptotic value.

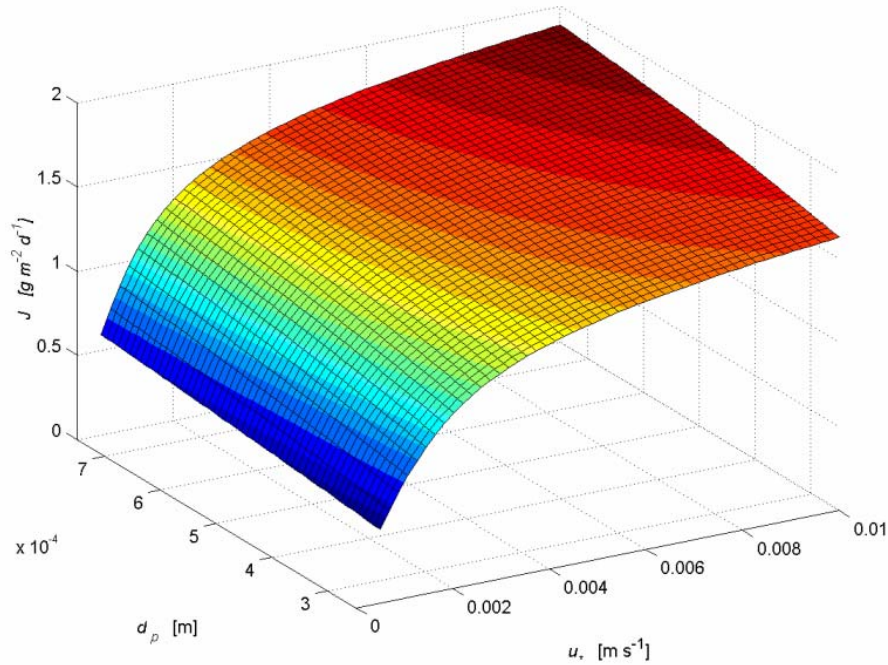


Fig 5 O<sub>2</sub> fluxes at the interface calculated with the variation of  $u_*$  and  $d_p$

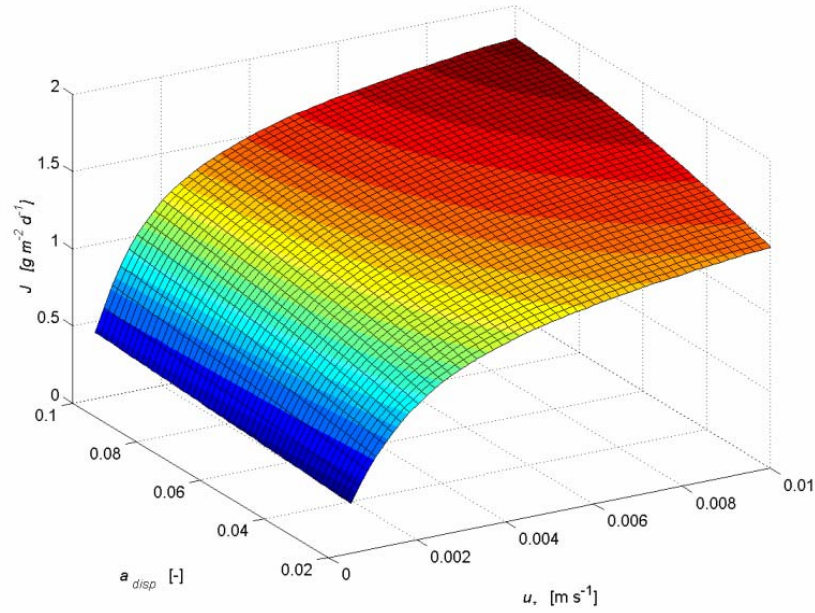


Fig 6  $\text{O}_2$  fluxes at the interface calculated with the variation of  $u_*$  and  $a_{\text{disp}}$

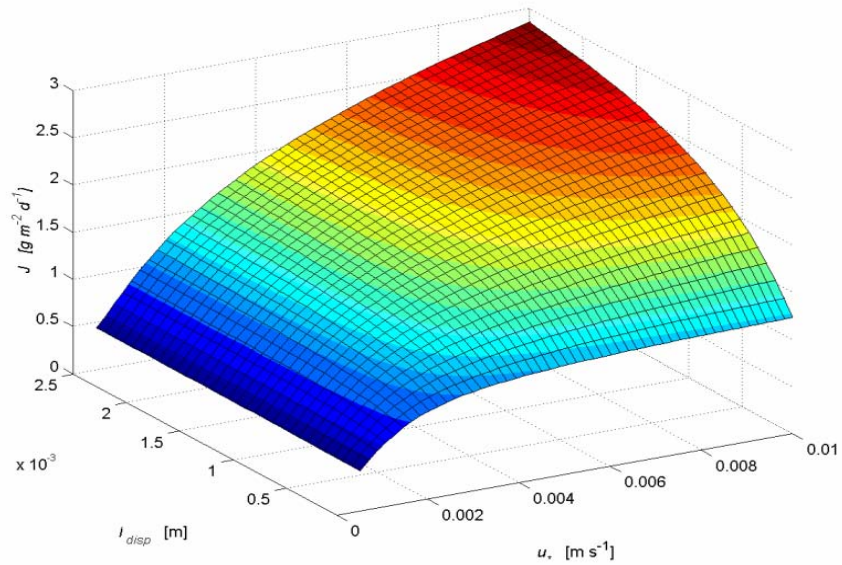


Fig 7  $\text{O}_2$  fluxes at the interface calculated with the variation of  $K_{\text{max}}$  and  $l_R$

## 5. Conclusions

Assuming the existence of a movement field, above the sediment layer, similar with the one generated by the 'wall hypothesis' in the past was often used the simplification of the problem to the calculus of a solute flux (at the sediment-water interface) combined with a 'fickian' model dominated only by the molecular diffusion. Some recent experiments, cited in the references [5, 6, and 7] describe the limits of such an approach. The purpose of this study was to evidence all the aspects of the transport process from the water column into the sediments, proposing an analytical model validated with experimental results; it was focused on the oxygen transport into the aquatic ecosystem.

It was distinguished as the most important parameter the attrition velocity specific to the movement above the interface that in the proposed closures, dictates the terms of turbulent or dispersive nature.

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