

SIMULATION OF LAKE'S SEDIMENTARY PHOSPHORUS BALANCE GOVERNED BY BIOIRRIGATION USING REACTIVE MULTI- COMPONENT TRANSPORT MODELING

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Summary. Oxygen is transported by bioirrigation into anoxic sediments and leads to an oxidation of iron, followed by precipitation processes. Phosphorus can be adsorbed onto the emerging mineral surfaces. Based on this conceptual geochemical approach a numerical reactive multi-component transport model including a surface complexation model was developed to simulate the impact of a macrozoobenthos species (*Chironomus plumosus*), which is living in small tubes in lake sediments. The model considers the relevant hydrodynamic and geochemical processes related to the activity of a given individual. Here, transport processes like diffusion and advection are of importance, and also degradation of organic matter, primary and secondary redox processes, mineral dissolution and precipitation, and sorption of phosphorus. Because of difficulties with sampling around the tubes the model calibration is based on a 1D laboratory experiment. The modeling results show that the model has the ability to reconstruct the biogeochemical processes in the sediment caused by aeration. In our case P sorption onto iron-oxyhydroxides not only depends on the pH but also on the composition of all ions capable for sorption.

1 INTRODUCTION

Due to intense biogeochemical turnover processes the benthic boundary layer is a hot spot regarding nutrient cycles. Studies quantifying limnic nutrient cycles are mainly focussing on nitrogen (N), and far less on phosphorus (P). However, in lakes of moderate climates P is usually the limiting factor for primary production. In numerous lakes macrozoobenthos has a severe impact on P turnover and retention [1], causing aeration of deeper sediment layers, which alters the net mineralisation and the syntheses of organic and inorganic compounds. Thereby it controls the early diagenetic processes in sediments [2].

A typical macrozoobenthos species in eutrophic lakes is *Chironomus plumosus* (Diptera: Chironomidae). The larvae perform bioirrigation by pumping water through their U-shaped

burrows in order to provide oxygen for respiration. As a result oxygen and other electron acceptors diffuse through the burrow into the surrounding sediment and lead to concentric redox zones around the burrow [3] and increased microbial degradation of organic matter [4][5]. Furthermore metabolites from mineralisation move from the sediment to the overlying water [2][6]. An important process concerning the P cycle is the precipitation of iron-oxyhydroxides in the aerobic zone followed by P adsorption onto these minerals.

Reactive transport models are useful to quantify P turnover and release. However, in studies of processes at the sediment-water-interface (SWI) either P was considered not at all [7] or with empirical P adsorption approaches [8][9][10][11][12]. The P adsorption depends on many factors, such as the pore water composition and the pH. The latter is considered to some extent in [12]. More sophisticated approaches are surface-complexation models (SCM), which consider the effects of variable chemical conditions on adsorption (for a review see [13]). Model calculations have shown the importance of such effects for metal adsorption [i.e. 14].

Our aim is to quantify the P cycle influenced by bioirrigation of *C. plumosus* larvae with a multi-component reactive transport model including a SCM approach. In the following we present first results of a non-steady state 1D model. The model calculations are based on a 1D laboratory experiment, where anaerobic sediment was aerated by overlying water. By means of such a simplified experimental design we avoided the difficulties with sampling of pore water around a burrow, caused by sharp chemical gradients near the burrow. Based upon the 1D model results a 2D radial model is planned for a real quantification of the P cycle around burrows of *C. plumosus* larvae.

2 MATERIAL & METHODS

The laboratory experiment was conducted with sediments and surface water from Lake Mueggelsee which is a shallow polymictic eutrophic lake in Berlin, Germany. A comprehensive description of the lake and its sediments is given in [15] and [16]. Sediment from 0 and 20 cm sediment depth was sieved to remove macrozoobenthos and subsequently homogenized. The experiment was realized in 3 aquariums, each with 15 cm lake sediment and 20 cm overlying lake water. For pore water sampling dialysis samplers [17] were installed, and the sampling was performed 2, 4 and 10 weeks after beginning of the experiment (one aquarium at each date). Dissolved oxygen was measured with a Clark-type oxygen micro electrode (Unisense, Denmark) every week. A fourth aquarium stocked up with *C. plumosus* larvae was taken only for sediment sampling. Here, sediment sampling was performed after 10 weeks, distinguishing between anaerobic sediment, aerobic sediment from the SWI and aerobic sediment from the burrow walls.

Table 1: Analysed pore water and sediment parameters

Pore water	Sediment
SRP (soluble reactive phosphorus), NH_4^+ , NO_3^- , DIC (dissolved inorganic carbon), DOC (dissolved organic carbon), Cl^- , SO_4^{2-} , dissolved Fe, dissolved Mn, Ca^{2+} , Na^+ , K^+	P fractionation [18], total iron, total manganese, C/N

With regard to the multi-component modeling those dissolved major ions were analyzed, which are reaction-relevant as well as necessary to realize an ion balance error below 5 %. Regarding the sediment analyses the focus was on parameters affecting the P adsorption. The measured parameters are listed in table 1.

3 MODEL FORMULATION

3.1 Diffusive transport

The 3D solute transport in sediment induced by bioirrigation of *C. plumosus* consists of diffusion and advection [19]. However, considering the boundary conditions in the 1D laboratory experiment, which means that the lower boundary is closed by the aquarium bottom, advection does not occur. That changes in case of a 2D radial or a 3D whole burrow model. In the model the diffusive flux is calculated using Fick's first law:

$$J_i = \frac{\varphi}{\Theta^2} \cdot D_i \cdot \frac{dC_i}{dz} \quad (1)$$

with J_i , diffusive flux of ion (i); φ , porosity of the sediment; Θ , tortuosity of the sediment; D_i , molecular coefficient of diffusion of i ; dC_i/dz , concentration gradient of i . The tortuosity can be calculated according to [8]:

$$\Theta = \sqrt{1 - \ln(\varphi^2)} \quad (2)$$

By reason of a porosity of about 95 % in the upper sediment [16] the term φ/Θ^2 in eq. (1) can be neglected. The molecular coefficient is set to $1 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for all dissolved species.

Table 2: Initial pore water and lake water composition used in model simulations

Parameters	Unit	Sediment pore water	Overlying lake water
chloride	[mmol·l ⁻¹]	1.3	1.3
sodium	[mmol·l ⁻¹]	1.22	1.305
calcium	[mmol·l ⁻¹]	2.42	2.44
magnesium	[mmol·l ⁻¹]	0.566	0.55
potassium	[mmol·l ⁻¹]	0.143	0.156
dissolved manganese	[mmol·l ⁻¹]	2.18e-2	0
nitrate	[mmol·l ⁻¹]	0	3.43e-2
ammonium	[mmol·l ⁻¹]	0.155	0
dissolved iron	[mmol·l ⁻¹]	6.45e-2	0
sulphate	[mmol·l ⁻¹]	0.7	1.7
sulphide	[mmol·l ⁻¹]	0	0
SRP	[mmol·l ⁻¹]	0.136	1.6e-3
TIC	[mmol·l ⁻¹]	2.78	2.2
pH	[-]	7.5	7.56
OM initial	[mol·l ⁻¹]	1	-
FeS initial	[mmol·l ⁻¹]	28.5	-
Calcite initial	[mmol·l ⁻¹]	3	-
Siderite	[-]	SI = 0.75	-
Rhodochrosite	[-]	SI = 0.56	-
Fe(OH) ₃ initial	[mmol·l ⁻¹]	10	-
Fe(OH) ₃ surface sites	mol mol ⁻¹ Fe	1	-
Fe(OH) ₃ surface area	m ² mol ⁻¹	53300	-

3.2 Boundary and initial conditions

According to the closed aquarium bottom in the experiment the lower model boundary is closed. The upper model boundary was set to a fixed concentration boundary according to the overlying lake water composition (Table 2). Due to an exposition time of the dialyse samplers of approximately 2 weeks an initial pore water sampling was not possible. Therefore, the initial pore water composition was estimated based on unpublished in situ data (Table 2).

3.3 Modeled components

In the first phase of modeling all available components in the Phreeqc standard database [20] were taken, as far as they are related to the measured species (Table 1). That covers dissolved aqueous complexes, minerals, and surface complexation components. Organic matter (OM) was implemented considering its main elements C, H, O, N and P. For an initial composition the Redfield ratio was chosen (C:N:P=106:16:1).

3.4 Reaction network and numerical implementation

In the laboratory experiment, biodegradation of OM was observed under aerobic, denitrifying, manganese- and iron-reducing conditions. The corresponding redox reactions are listed in [9, eq. 1 – 4]. OM mineralization by dissolved oxygen, MnO_2 and $\text{Fe}(\text{OH})_3$, was considered to be kinetically controlled and described by a simplified Monod-type rate expression [12]:

$$R_{OM} = \sum_{i=1}^n r_{\max,i} \frac{C_i}{C_i + C_i^{\text{lim}}} \prod_{j=1}^{i-1} \frac{C_j^{\text{inh}}}{C_j + C_j^{\text{inh}}} \quad (3)$$

for $i = \{\text{O}_2, \text{MnO}_2, \text{Fe}(\text{OH})_3, \text{SO}_4^{2-}\}$ and $j = i+1$, with R_{OM} , overall degradation rate of OM; $r_{\max,i}$, maximum rate constant for the respective species; C_i , concentration of the terminal electron acceptors (TEA); C_i^{lim} , Monod constant; C_i^{inh} , inhibition constant. Due to its small amount, for nitrate a local equilibrium approach (LEA) is assumed. Non-redox mineral precipitation and dissolution reactions are considered for calcite, siderite, rhodochrosite and FeS (as FeS(ppt) in the Phreeqc database). LEA is applied to these mineral reactions, except for calcite, as well as to secondary redox and acid-base reactions. The dissolution/precipitation kinetics of calcite is implemented according to [21]. The coherent database from [22] for surface complexation on hydrous ferric oxide was considered in the model. The reaction network was incorporated to the geochemical model code Phreeqc-2 [20]. In Phreeqc-2 the OM oxidation reactions can be linked with eq. 3 by applying the partial equilibrium approach (PEA) [23]. With the use of the PEA the TEA's are automatically consumed in the order of their thermodynamic favourability.

3.5 Model calibration and verification

Due to the 3 temporal discrete sampling events it is possible to calibrate the model based on the measured species of the first sampling event, and to verify it based on the measured values of the second and third one. A trial-and-error fitting procedure was applied including all measured species. The maximum rates, Monod constants and inhibition constants in eq. 3 were modified to achieve a good fit. Equilibrium constants from the Phreeqc standard database are not treated as adjustable parameters. Subsequently we present the results of the first modeling step, meaning the best fit of the measured parameters to date from the first sampling event.

4 RESULTS AND DISCUSSION

In principal at the SWI the anaerobic sediment indicates a small oxic zone (4.5 mm) followed by a nitrate-reducing zone (Fig. 1). The anaerobic zone below is characterized by overlapping manganese and iron-reducing conditions. The measured sulphate profile indicates that no sulphate reduction occurred; that the profile is only controlled by diffusion. First fitting results are also shown in Fig. 1. The model reproduces the concentration profile of dissolved oxygen. The modeled nitrate-reducing zone reaches too deep into the sediment. Accordingly, the transition to manganese and iron-reducing conditions starts too deep.

In the model, we assumed that the ammonium release is only coupled to OM degradation. The discrepancy between measured and modeled ammonium concentration is therefore either caused by underestimated OM degradation under iron reducing conditions, or the OM composition does not correspond to the Redfield ratio, i.e. the OM nitrogen content is underestimated in the model. With a higher OM degradation rate the modeled phosphorus concentration would be higher than the measured one, because of an additional release of phosphorus from OM degradation as well as desorption caused by $\text{Fe}(\text{OH})_3$ reduction. Therefore it is essential to measure the real stoichiometric C-N-P ratio of the OM. Questionable is the relevance of that issue for the P adsorption onto fresh $\text{Fe}(\text{OH})_3$ originating from the oxidation of ferric iron after oxygen input. With an increased ammonium release in the anaerobic zone presumably the modeled iron-reducing zone would shift closer to the SWI. Thus the fit of dissolved iron, dissolved manganese, and nitrate would be improved. Hence the $\text{Fe}(\text{OH})_3$ precipitation zone and consequently the amount of potential sorption sites for P would be diminished. The current sorption capacity of the fresh $\text{Fe}(\text{OH})_3$ at the SWI is approximately $300 \mu\text{mol}/\text{dm}^2$ (calculated from the amount of fresh $\text{Fe}(\text{OH})_3$ and its surface sites in Table 2). With the numerical procedure of [24] a P production of $40 \mu\text{mol dm}^{-2}$ in the anaerobic zone was calculated for a period of 2 weeks. Owing to diffusion these P moves to the SWI and will be sorbed to the fresh $\text{Fe}(\text{OH})_3$. This is also reflected by an increase of sorbed P near the SWI. Compared to the calculated sorption capacity only 13 % of the sorption sites of the fresh $\text{Fe}(\text{OH})_3$ are occupied by P. As shown in Fig. 2 the most competing ions due to the sorption are protons and bicarbonate, and to a lesser extent magnesium. This means that the P sorption depends not only on the pH, as assumed by other authors (e.g. [12]), but also on the chemical composition of the pore water.

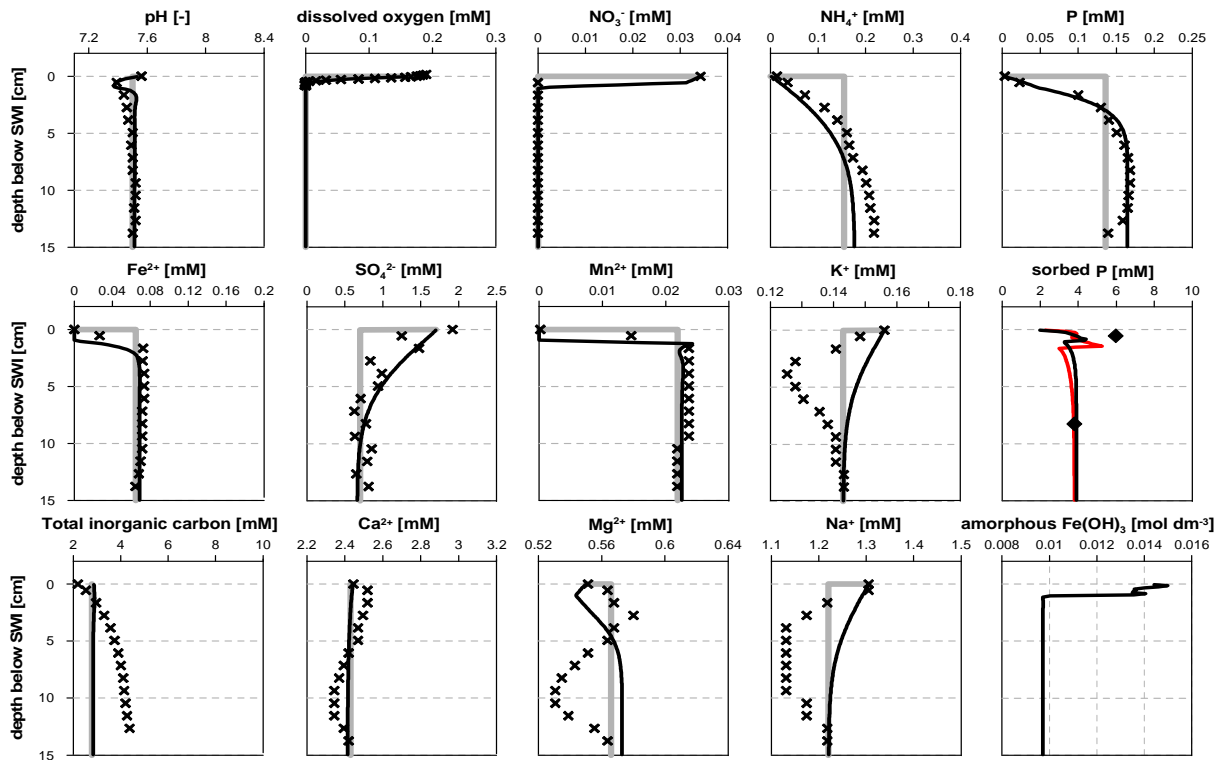


Figure 1 : Depth profiles of the measured and modeled dissolved, sorbed and solid components. The measured values come from the first sampling event 2 weeks after the beginning of the experiment (except for the measured sorbed phosphorus, which was measured after 10 weeks). x measured values; — modeled values (2 weeks); — initial values in the model; — modeled values (10 weeks); ♦ measured value (10 weeks)

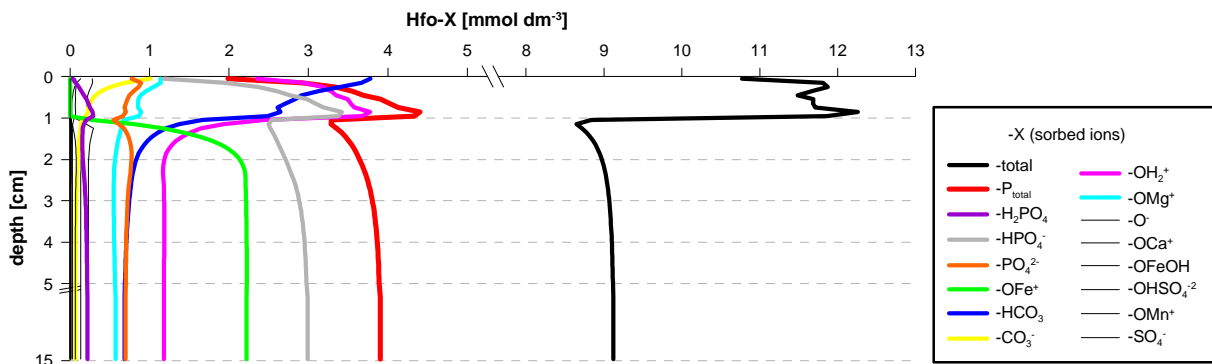


Figure 2 : Depth profiles of the modeled sorbed components

At the moment the calibrated model time is 2 weeks. To test the validity of the model with the measured sorbed P we simulated 10 weeks. As one can see in Figure 1 the modeled concentration of sorbed P is a little smaller than the measured concentration. The pH fit is surprisingly well. In the model the pH in the anaerobic zone is controlled mainly by siderite.

Siderite also controls the concentration of dissolved iron, while dissolved manganese is controlled by rhodochrosite. Only in a depth between 1 and 4 cm there is a pH discrepancy. Feasible reasons could be lacking secondary redox kinetics in the database, instead of an as yet simulated LEA. To date there is no agreement between measured and modeled TIC as well as the dissolved alkaline and alkaline earth metals. Regarding TIC further model calibration is necessary. Calcium, magnesium, sodium and potassium are subject to cation exchange, which is not implemented into the model. When focussing on P, a sufficient fitting of these cations is only necessary if they influence the composition of sorbed ions at the fresh $\text{Fe}(\text{OH})_3$. In the current model fit that applies in a small part to magnesium (Fig. 2).

5 CONCLUSIONS

The results demonstrate that a reactive multi-component model including a SCM has the ability to simulate the aeration induced biogeochemical processes at the SWI of a lake. We show that the P sorption onto iron-oxyhydroxides not only depends on the pH but also on the composition of all ions capable for sorption. For a proper quantification of the influence of the aeration on P release from the sediment a further model adjustment is necessary.

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