

A model study of the effects of sulfide-oxidizing bacteria (*Beggiatoa* spp.) on phosphorus retention processes in hypoxic sediments: Implications for phosphorus management in the Baltic Sea

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Received 14 June 2010, accepted 23 Nov. 2010 (Editor in charge of this article: Heikki Seppä)

Yekta, S. S. & Rahm, L. 2011: A model study of the effects of sulfide-oxidizing bacteria (*Beggiatoa* spp.) on phosphorus retention processes in hypoxic sediments: Implications for phosphorus management in the Baltic Sea. *Boreal Env. Res.* 16: 167–184.

Ongoing eutrophication increases phosphorus storage in surficial sediments of the Baltic Sea which can then be released during hypoxic/anoxic events. Such sediments are suitable habitats for sulfide-oxidizing bacteria, *Beggiatoa* spp. The objective of this paper is to investigate the effects of these bacteria on the P retention processes in hypoxic sediments using a diagenetic model. This model simulates interactions of the processes controlling P mobility in the sediments with redox reactions from the *Beggiatoa* metabolism. Modeling results demonstrate that P retention capability is limited when dissolved iron is mineralized as iron sulfides in the sediments. In this regard, sulfide consumption by *Beggiatoa* spp. potentially decreases the rate of iron sulfide formation and consequently increases the P retention capability in local-scale sediment.

Introduction

Surficial sediments of the Baltic Sea contain amounts of phosphorus (P) comparable to many years of riverine loads (Conley *et al.* 2002). This P source can be released during hypoxic/anoxic events and in a longer perspective may fuel nitrogen (N)-fixing cyanobacteria blooms and render remedy actions based on reduction of N loads less successful (Cloern 2001). In fact, the portion of hypoxic/anoxic sediments increased not only relatively but also quantitatively during the recent decades in the Baltic Sea. This increase seems to be a global phenomenon (Diaz and Rosenberg 2008). However,

during the middle of the 1990s, mild windy winters led to an increased mixing of the water column, less hypoxic/anoxic bottoms, and a drastic drop in P concentration in the water mass (Gustafsson and Stigebrandt 2007). This inspired the development of new remedy processes by improving the oxygen conditions in the bottom layers and thereby increasing P retention in the sediments based on increased concentrations of Fe(III) oxides (Mortimer 1941). Knowledge of the processes at the sediment water interface regulating the hypoxic/anoxic sediments is crucial in these attempts.

Hypoxic/anoxic bottoms eliminate higher orders of life but make the new sediment sur-

face a suitable habitat for sulfide-oxidizing bacteria, *Beggiatoa* spp. (Rosenberg and Diaz 1993). *Beggiatoa* cells build aggregates in sediments rich in organic matter with a gradient of sulfide across the sediment water interface (Mußmann *et al.* 2003). These bacteria are chemoautotrophs, gaining metabolic energy by oxidizing hydrogen sulfide (Jørgensen 1982). Widespread *Beggiatoa* mats have been observed in the Stockholm Archipelago (Rosenberg and Diaz 1993), in anoxic sediments of the Gulf of Finland (Vallius 2006), and in huge areas of the eastern Gotland basin (P. Hall, Gothenburg University, pers. comm.). The Danish Limfjorden, the German Wadden Sea and Eckenförde Bay are other examples where large populations of these bacteria have been observed (Mußmann *et al.* 2003, Preisler *et al.* 2007).

Beggiatoa spp. is well-known for protecting overlying water from toxic sulfide diffused from the sulfidic layers of the sediments. *Beggiatoa* metabolism including their physiology and enzymology have been studied in detail (e.g. Jørgensen 1977, Hagen and Nelson 1997, Mußmann *et al.* 2003, Sayama *et al.* 2005, Hinck *et al.* 2007, Kamp *et al.* 2008). Furthermore, the role of these bacteria in the cycling of elements has been the topic of numerous studies. As an example, Fenchel and Bernard (1995) investigated major microbial processes such as nitrification/denitrification and cycling of N in a *Beggiatoa* inhabited sediment. Preisler *et al.* (2007) studied sulfide oxidation by *Beggiatoa* mats and its interactions with manganese and iron in local scale sediment. Most of the previous studies emphasized the importance of these bacteria in the cycling of elements in marine environments, but to our knowledge, none of the earlier studies investigated the impact of *Beggiatoa* spp. on P retention processes in their growth medium.

Phosphorus (P) retention processes in the sediments of the Baltic Sea have been amply researched. For instance, Brüggmann *et al.* (1992), Sternbeck and Sohlenius (1997), Hille *et al.* (2005), and Leipe *et al.* (2008) have all contributed to knowledge in this area. Previous studies showed that mobility of P in the sediment-porewater medium is chiefly regulated by adsorption of phosphate on iron oxyhydroxides.

Dissolution of iron oxide sheets to Fe^{2+} in the top layers of the sediments caused by shifts from oxic to hypoxic/anoxic conditions in bottom water, changes the sorption capability of the sediments and leads to mobilization of iron-bound phosphate which can be transferred to overlying water columns (Conley *et al.* 2002).

To understand the effects of *Beggiatoa* mats on P retention processes, we developed a diagenetic model for reactive diffusive transport of substances to simulate major biogeochemical processes in the sediments like those in the Baltic Sea with both *Beggiatoa*-free and *Beggiatoa*-covered sediment surfaces. The *Beggiatoa*-free sediment model couples biotic processes such as organic matter degradation pathways with inorganic processes including iron oxide precipitation/dissolution, iron sulfide precipitation, and P adsorption/desorption. Organic matter degradation pathways are the main contributors to redox disequilibrium in the sediments (Tromp *et al.* 1995), while inorganic processes are the major chemical pathways controlling mobility of P in marine sediments (Jensen *et al.* 1995, Carman and Rahm 1997, Gunnars *et al.* 2002, Conley *et al.* 2002, Lehtoranta and Pitkänen 2003, Lehtoranta *et al.* 2008). In the next step, we added microbially mediated redox reactions from the *Beggiatoa* metabolism to the model in order to simulate their interactions with sedimentary processes. The development and application of diagenetic models for the investigation of sedimentary processes can be found in e.g. Berner (1964), Boudreau (1997), and Boudreau and Jørgensen (2001).

The current model simulates the key P retention processes in natural sediments based on observations and field measurements of water and sediments of the Baltic Sea. Through modeling, we do not intend to reproduce the observed data but to provide a realistic numerical representation of the sedimentary processes. The goal of the study is to investigate our conceptual understanding of the impact of *Beggiatoa* mats on the P retention processes in sediments by comparing two conventional diagenetic models simulating typical Baltic Sea hypoxic sediments which differ only in the presence or absence of *Beggiatoa* mat.

Material and methods

We developed a 1D diagenetic model to simulate the vertical distribution of solute and solid compounds in local scale sediment. In doing this, we treated sedimentary solute and solid species (Fig. 1) as dependent variables and considered their mass conservation equations in an arbitrary sediment system. We included chemical reaction pathways in conservation equations as sources or sinks to simulate dynamic interactions of dissolved and solid compounds. Boudreau and Jørgensen (2001) discussed derivation of mass conservation equations for sedimentary substances and biogeochemical processes in detail.

Model conceptualization

Model conceptualization including incorporated biochemical reactions is illustrated in Fig. 1. The model simulates an arbitrary vertical column of a sediment–porewater system with a given geometry. The present model simulates the distribution of dissolved and solid compounds from the mixed water body downwards across the diffusive boundary layer (DBL) and into the sediment–porewater medium. The model was allowed to spin up during a simulation period of four years which is long enough to produce quasi-steady concentration profiles by time. We also applied field data from porewater analysis of three hypoxic sediments (Carman and Rahm

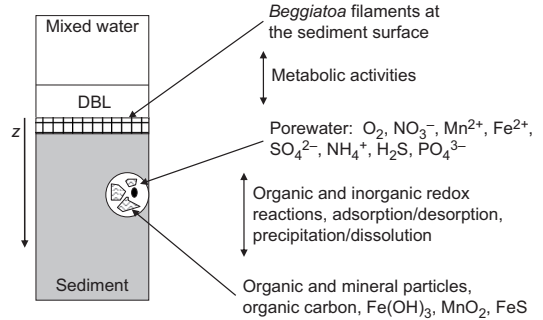


Fig. 1. Model conceptualization and incorporated biochemical processes in the modeled sediment column. z represents sediment depth.

1997) in order to compare simulated and measured concentration profiles and adjusted some model parameters to approach the measured profiles. This provided us with a numerical tool for further investigations of the P retention processes as well as the effects of *Beggiatoa* mats on them.

Physical model properties

The physical properties of the model are listed in Table 1. We fixed the model geometry as a vertical sediment column with a depth of 20 cm. The system was divided into layers of 0.1 cm thickness. The thin layers were required to capture steep gradients below the surface sediment. A time step of six hours was chosen. Decreasing the time step to less than six hours did not

Table 1. Physical parameters of the model. Explanations: μ is the dynamic viscosity, V_b is molar volume of the nonelectrolyte, m_0 and m_1 are experimentally measured linear regression coefficients for calculation of diffusion coefficients of cations and anions against temperature (τ , °C) based on the Nernst-Einstein expression, T is the temperature in kelvins (K). Values for these parameters are found in Boudreau (1997).

Parameter	Value or formula (unit)	Source
Sediment depth	20 (cm)	
Length of iterations	0.1 (cm)	
Length of time steps	6 (hr)	
Simulation period	4 (yr)	
Porosity	$\phi = 0.8$	Carman and Rahm (1997)
Sedimentation rate	$w = 0.1$ (cm yr ⁻¹)	Hille <i>et al.</i> (2006)
Tortuosity	$\theta^2 = 1 - \ln\phi$	Tsai and Strieder (1986)
Biodiffusion coefficient	$D_B = 15.7w^{0.69}$ (cm ² yr ⁻¹)	Boudreau (1997)
Diffusivity of molecules in water	$D_{\text{molecular}} = 4.72 \times 10^{-9} [T(\mu V_b)^{-0.6}]$ (cm ² yr ⁻¹)	Hayduk and Laudie (1974)
Diffusivity of ions in water	$D_{\text{ionic}} = (m_0 + m_1\tau) \times 10^{-6}$ (cm ² yr ⁻¹)	Boudreau (1997)

change the simulated profiles of the compounds. Hille *et al.* (2006) estimated the mean linear sedimentation rate of roughly $0.1 \text{ (cm yr}^{-1}\text{)}$ for the Gotland basin. We calculated diffusion coefficients of porewater species according to the formula derived for the diffusion of corresponding molecules or ions in the water (Table 1) and modified their values for a porous medium by including the parameter of tortuosity. This parameter considers the longer distances that a molecule has to travel in a porous medium compared to water. We used the average values of bottom water composition from the three hypoxic stations studied by Carman and Rahm (1997) in order to estimate both the upper boundary conditions and the initial values of the model variables (Table 2). Organic and inorganic reactions and the rationale for choosing them are described in the following subsections.

Organic matter degradation processes

Organic detritus from the water column is the energy source for diverse microorganisms living

Table 2. Upper boundary conditions and initial values of sediment and porewater compounds.

Dissolved compound	^a Bottom water concentration (μM)
O_2	91
NO_3^-	10.27
Mn^{2+}	0 ^b
Fe^{2+}	0 ^b
SO_4^{2-}	8500
NH_4^+	0.38
H_2S	0
PO_4^{3-}	2.41
Solid compound	^c Deposition rate ($\mu\text{mol cm}^{-2} \text{ yr}^{-1}$)
Organic C	2500
$\text{Fe}(\text{OH})_3$	60
MnO_2	40
FeS	0

^a Average values of bottom water concentrations from Carman and Rahm (1997)

^b From Canfield *et al.* (1993).

^c Deposition rates were adjusted for calibration purposes and initial values of the solid compounds are assumed zero.

beneath the sediment–water interface. Organic matter degradation with multiple electron acceptors is the most important microbial process controlling redox conditions in the sediments (Tromp *et al.* 1995). In the current model, we considered plankton decomposition as the ultimate energy supply for the microbial community (Redfield 1958). In general, over 90% of deposited organic matter is oxidized in the upper layers of the sediments (15–20 cm), and only a small, inert fraction is permanently buried (Jørgensen 1982, Boudreau 1997). The rates of different organic carbon oxidization pathways primarily depend on the types of available organic matter in terms of reactivity. Reactive organic matter is easily degraded while the refractory fraction is resistant to microbial assimilation and consequently, its degradation rate is lower than the reactive fraction (Tromp *et al.* 1995). We applied first order kinetics for the oxidization rate of organic matter (Berner 1964, Canfield *et al.* 1993, Tromp *et al.* 1995, Van Cappellen and Wang 1996):

$$R_{\text{O}} = kC_{\text{orgC}} \quad (1)$$

where C_{orgC} is the concentration of organic carbon and k is the generic rate constant for reactive (k_{reactive}) and refractory ($k_{\text{refractory}}$) organic carbon calculated according to formula reported by (Tromp *et al.* 1995):

$$k_{\text{reactive}} = 2.97w^{0.62} \quad (2)$$

$$k_{\text{refractory}} = 0.05w^{1.94} \quad (3)$$

where w is the linear sedimentation rate. In marine sediments, electron acceptors with higher Gibbs free energy suppress the reactions of oxidants with lower Gibbs free energy (Van Cappellen and Wang 1996). In oxic layers, oxygen, as the most powerful oxidant, is responsible for organic matter degradation through the respiration of aerobes. Depletion of oxygen favors other electron acceptors and shifts the organic carbon oxidization pathway from aerobic respiration to denitrification and subsequently to Mn and Fe oxide reduction, sulfate reduction and methanogenesis. These processes are listed in (Table 3).

Sequential inhibition of organic carbon oxidization pathways by more powerful electron

Table 3. Chemical expressions of organic matter degradation pathways (Redfield 1958, Tromp *et al.* 1995, Van Cappellen and Wang 1996).

Pathway	Stoichiometry of reaction
R1: Aerobic respiration	$G + (x + 2y)O_2 + (y + 2z)HCO_3^- \rightarrow (x + y + 2z)CO_2 + (x + 2y + 2z)H_2O + yNO_3^- + zHPO_4^{2-}$
R2: Denitrification	$5G + (4x + 3y)NO_3^- \rightarrow (x - 3y + 10z)CO_2 + (3x + 6y + 10z)H_2O + (4x + 3y - 10z)HCO_3^- + (2x + 4y)N_2 + 5zHPO_4^{2-}$
R3: Mn oxide reduction	$G + 2xMnO_2 + (3x + y - 2z)CO_2 + (x + y - 2z)H_2O \rightarrow 2xMn^{2+} + (4x + y - 2z)HCO_3^- + yNH_4^+ + zHPO_4^{2-}$
R4: Fe oxide reduction	$G + 4xFe(OH)_3 + (7x + y - 2z)CO_2 \rightarrow 4xFe^{2+} + (8x + y - 2z)HCO_3^- + yNH_4^+ + (3x - y + 2z)H_2O + zHPO_4^{2-}$
R5: Sulfate reduction	$G + (x/2)SO_4^{2-} + (y - 2z)CO_2 + (y - 2z)H_2O \rightarrow (x/2)H_2S + (x + y - 2z)HCO_3^- + yNH_4^+ + zHPO_4^{2-}$
R6: Methane production	$G + (y - 2z)H_2O \rightarrow (x/2)CH_4 + [(x - 2y - 4z)/2]CO_2 + (y - 2z)HCO_3^- + yNH_4^+ + zHPO_4^{2-}$

G: Plankton composition, $(CH_2O)_x(NH_3)_y(H_3PO_4)_z$; $x = 106$, $y = 16$, $z = 1$.

acceptors can be included into diagenetic models by the introduction of “inhibition constants” to the rate equations of organic matter degradation (e.g. Boudreau and Westrich 1984, Tromp *et al.* 1995). To avoid overparameterization of the model due to the application of this approach, we implemented a decision algorithm in the computer program to shift the oxidization pathways while the pool of an electron acceptor with higher oxidization power is depleted in the sediment medium (Van Cappellen and Wang 1996). We assumed that organic matter decomposition does not occur via two simultaneous processes except for nitrate reduction which occurs under both aerobic and anaerobic conditions (Robertson and Kuenen 1984). The limiting effects of the concentration of porewater electron acceptors on corresponding organic degradation pathways are incorporated by including the Monod kinetics term into the organic carbon oxidization rate:

$$R_i = R_o \frac{C_i}{K_{Si} + C_i} \quad (4)$$

Table 4. Modeled values of saturation constants for different organic matter degradation pathways.

Reaction number	Saturation constant	Unit
R1	$K_{S,O_2} = 40$	μM
R2	$K_{S,NO_3^-} = 10$	μM
R3	$K_{S,MnO_2} = 50$	$\mu mol\ g^{-1}$
R4	$K_{S,Fe(OH)_3} = 200$	$\mu mol\ g^{-1}$
R5	$K_{S,SO_4^{2-}} = 4$	mM

where R_o is the first order oxidization rate of organic carbon (Eq. 1), C_i is the concentration of the limiting electron acceptor i (i.e. O_2 , NO_3^- , MnO_2 , $Fe(OH)_3$, SO_4^{2-}), and K_{Si} is the corresponding saturation constant. We treated the saturation constants as model parameters and used them for calibration purposes (Table 4).

Inorganic processes

The model couples organic carbon oxidization to inorganic reactions. In particular, we incorporated the most important P retention processes in the model (Table 5). In the sediments, iron oxides, as the main P-bearing minerals, are microbially (Table 3: R4) and chemically (Table 5:

Table 5. Inorganic reaction network in the modeled sediment (Van Cappellen and Wang 1996, Boudreau 1997).

Stoichiometry of reaction
R7: $H_2S + 2Fe(OH)_3 + 4CO_2 \rightarrow 2Fe^{2+} + 4HCO_3^- + S^0 + 2H_2S$
R8: $H_2S + MnO_2 + 2CO_2 \rightarrow Mn^{2+} + 2HCO_3^- + S^0$
R9: $H_2S + 2O_2 + 2HCO_3^- \rightarrow SO_4^{2-} + 2CO_2 + 2H_2O$
R10: $Fe^{2+} + 1/4O_2 + 2HCO_3^- + 1/2H_2O \rightarrow Fe(OH)_3 + 2CO_2$
R11: $Mn^{2+} + 1/2O_2 + 2HCO_3^- \rightarrow MnO_2 + 2CO_2 + H_2O$
R12: $2Fe^{2+} + MnO_2 + 2HCO_3^- + 2H_2O \rightarrow 2Fe(OH)_3 + Mn^{2+} + 2CO_2$
R13: $NH_4^+ + 2O_2 + 2HCO_3^- \rightarrow NO_3^- + 2CO_2 + 3H_2O$
R14: $Fe^{2+} + 2HCO_3^- + H_2S \leftrightarrow FeS + 2CO_2 + 2H_2O$

R7) reduced to ferrous ions by iron(III)-reducer bacteria and sulfide respectively. In oxic parts, ferrous ions are mineralized by oxygen (Table 5: R10) and freshly precipitated iron oxides adsorb porewater phosphate (Sobolev and Roden 2001). Furthermore, Mn oxides increase the efficiency of the iron oxide precipitation process through their reductive dissolution by ferrous ions (Table 5: R12) (Myers and Neelson 1988). The precipitation/dissolution of iron sulfide minerals is described in (Table 5: R14). The process depends on the surface area and roughness of the mineral phase as well as the chemical effects of the porewater composition which are incorporated in the rate constants of the reactions (Rickard 1995).

We applied bimolecular kinetics to correlate the rates of homogeneous and heterogeneous inorganic reactions with the porewater concentration of redox couples (Van Cappellen and Wang 1996):

$$R_{\text{Ox,Rd}} = k_{\text{Ox,Rd}} C_{\text{Ox}} C_{\text{Rd}} \quad (5)$$

where $k_{\text{Ox,Rd}}$ is the rate constant and C is the concentration of denoted oxidant (Ox) and reductant (Rd). Rate constants from Van Cappellen and Wang (1996) were used as reference values and we adjusted the rate constants so the modeled profiles of the sedimentary substances would correspond with the observed trends (Table 6). It is noted that the calibrated kinetic parameters reflect the model's uncertainties and simplifying assumptions hence they are not applicable in other studies as information for individual chemical processes.

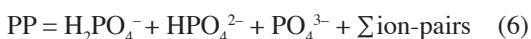
Table 6. Rate constants of inorganic reactions.

Reaction number	Adjusted value	Value from (Van Cappellen and Wang 1996) ($\mu\text{M}^{-1} \text{yr}^{-1}$)
R7	$K_{\text{H}_2\text{S,Fe(OH)}_2} = 0.015$	≤ 0.1
R8	$K_{\text{H}_2\text{S,MnO}_2} = 0.0015$	≤ 0.01
R9	$K_{\text{H}_2\text{S,O}_2} = 0.36$	≥ 0.16
R10	$K_{\text{Fe}^{2+},\text{O}_2} = 140$	140
R11	$K_{\text{Mn}^{2+},\text{O}_2} = 10$	0.8–20
R12	$K_{\text{Fe}^{2+},\text{MnO}_2} = 15$	≤ 1000
R13	$K_{\text{NH}_4^+,\text{O}_2} = 3$	10
R14	$K_{\text{Fe}^{2+},\text{H}_2\text{S}} = 300$	No data

P adsorption

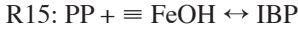
Adsorption of various porewater phosphate (PP) species on the sorption sites of iron oxide minerals and formation of iron-bound phosphate (IBP) species is the main reaction controlling the mobility of P in the Baltic Sea sediments (Jensen *et al.* 1995, Conley *et al.* 2002, Gunnars *et al.* 2002, Lehtoranta *et al.* 2008). Several studies tried to identify various PP and IBP species in this process (e.g. Tejedor-Tejedor and Anderson 1990, Persson *et al.* 1996, and Gao and Mucci 2003). According to these studies, PP includes compounds from the dissociation of phosphoric acid (H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-}) as well as a variety of ion-pairs formed between these substances and porewater cations (e.g. MgHPO_4 , $\text{CaH}_2\text{PO}_4^+$, and NaPO_4^{2-}). IBP includes monodentate and bidentate surface complexes formed through interactions of PP species with hydroxyl groups of ferric oxide minerals [e.g. FeH_2PO_4 and $(\text{FeO})_2\text{PO}_4^-$].

In a multicomponent electrolyte system like the sediment-water medium, porewater properties such as pH, ionic strength, and the presence of competitive adsorbents influence the distribution of phosphate between sediment mineral and porewater phases. Furthermore, types of iron oxide particulates (e.g. ferrihydrite, goethite and hematite), their availability, structure, and sorption affinity are influential on the adsorption/desorption of phosphate (Geelhoed *et al.* 1997, Gao and Mucci 2001, Spiteri *et al.* 2008). To simplify this complexity, we applied the main features of the adsorption equilibrium herein. It is assumed that iron oxide minerals have an equal potential for P sorption and a homogeneous surface with hydroxyl groups being the only active surface functional group. The model defines the parameters of PP and IBP as representatives for all porewater and iron-bound P species respectively, irrespective of their particular type:



where the symbol \equiv represents sorption sites on the surface of iron oxide minerals. The model assumes equilibrium adsorption/desorption reac-

tions which implies the rate of these reactions are fast relative to reactive diffusive transport of substances in the sediment (Spiteri *et al.* 2008):



We used the equilibrium isotherm to describe the partitioning of porewater and iron-bound fractions of phosphate:

$$C_{\text{IBP}} = K_p C_{\text{PP}} C_{\equiv \text{FeOH}} \quad (8)$$

where C is the concentration of the denoted solute and solid substances, and K_p is termed as the overall equilibrium constant and treated as a model parameter (with the calibrated value of $10^{2.5}$). Recall that the present P adsorption model neither considers the types of surface complexes and dissolved species nor their individual adsorption equilibrium. Furthermore, the introduced reaction (R15) represents the overall adsorption equilibrium instead of specifying this process for individual solid and solute phosphate species. K_p incorporates the effects of pH, ionic strength and surface charging on the availability of free surface sites for P adsorption. According to the presented adsorption scheme, fractions of PP and IBP and their correlation with available sorption sites ($C_{\equiv \text{FeOH}}$) are determined as follow:

$$\lambda_{\text{TP}} = \frac{C_{\text{PP}}}{C_{\text{PP}} + C_{\text{IBP}}} = \frac{1}{1 + K_p C_{\equiv \text{FeOH}}} \quad (9)$$

$$\lambda_{\text{IBP}} = \frac{C_{\text{IBP}}}{C_{\text{PP}} + C_{\text{IBP}}} = 1 - \lambda_{\text{TP}} \quad (10)$$

We termed λ_{PP} and λ_{IBP} as the distribution coefficients for porewater and iron-bound phosphate species respectively, which quantify PP and IBP fractions in any given depth of the sediment according to available sorption sites.

Since we intended to investigate the major P retention processes in the sediments, less influential processes such as adsorption of phosphate on other sedimentary particulates like Mn oxides and the formation of authigenic P-containing minerals (Ruttenberg and Berner 1993) were not considered. The latter was negligible in analyzed sediments of the Baltic Sea by Carman and Rahm (1997). Hence, total phosphate (TP) in the modeled sediment system is the summation of

dissolved and iron-bound forms:

$$C_{\text{TP}} = C_{\text{PP}} + C_{\text{IBP}} \quad (11)$$

The conservation equation for this variable is derived by summing mass conservation equations of PP and IBP as follows:

$$\frac{\partial C_{\text{TP}}}{\partial t} = \frac{\partial}{\partial z} \left(\frac{D_{\text{PP}}}{\theta^2} \frac{\partial (\lambda_{\text{TP}} C_{\text{TP}})}{\partial z} + D_{\text{B}} \frac{\partial C_{\text{TP}}}{\partial z} \right) - w \frac{\partial C_{\text{TP}}}{\partial z} + \sum R_p \quad (12)$$

where t is time, z vertical coordinate (depth), C concentration of denoted species, w sedimentation rate, θ tortuosity, $\sum R_p$ the sources and sinks of TP in form of chemical reactions, and D_{B} the biodiffusion coefficient (*see* Table 1). D_{PP} is the diffusion coefficient of dissolved phosphate species including ion pairs calculated according to the formula reported by Krom and Berner (1980):

$$D_{\text{PP}} = 112(1 + 0.048\tau) \quad (13)$$

where τ is ambient temperature of sediment-water system in °C.

Beggiatoa metabolism

The current model couples microbially mediated redox reactions from the *Beggiatoa* metabolism with sedimentary multicomponent reactions (Fig. 1). According to early studies of *Beggiatoa* spp., these microorganisms are characterized by their sulfide oxidation capability, internal sulfur vacuoles and gliding motility. They obtain metabolic energy by the aerobic oxidation of sulfide to internal sulfur and/or sulfate. They use their gliding motility to trace the oxic/anoxic interface as a way for balancing fluxes of sulfide and oxygen across their micrometer scale habitat (Jørgensen 1982, Jørgensen and Revsbech 1983, Nelson *et al.* 1986).

More recently, *Beggiatoa* enzyme analyses demonstrated that the biomass of these microorganisms contains respiratory nitrate reductase which enables them to use nitrate as an electron acceptor for sulfide oxidation (McHatton *et al.*

1996). *Beggiatoa* filaments are able to internally accumulate nitrate in levels up to four orders of magnitude higher than the nitrate concentration of their surrounding porewater (Mußmann *et al.* 2003) and to use intracellularly stored nitrate for sulfide oxidization. *Beggiatoa* nitrate storing ability together with their gliding motility enables them to trace and take up sulfide in anoxic parts of the sediments and expand their living environment from the micrometer to the centimeter scale (Kamp *et al.* 2006).

Beggiatoa filaments integrate gliding motility with nitrate and sulfur storage to efficiently scavenge substrates from the environment. When oxygen and nitrate are available, *Beggiatoa* filaments perform sulfide oxidization with two spatially separated pathways (Table 7). *Beggiatoa* filaments store nitrate intracellularly (Table 7: R16), in vacuoles or possibly cytoplasm (Kamp *et al.* 2006) and transport it downwards to anoxic sediment layers via their gliding mechanism. Transported nitrates are used for anaerobic sulfide oxidization to elemental sulfur (Table 7: R17) which will then be stored in vacuoles for aerobic oxidization to sulfate in oxic parts of the bacterial mat (Table 7: R18) (McHatton *et al.* 1996, Sayama *et al.* 2005, Kamp *et al.* 2006).

The model implements the chemical mechanism proposed by Sayama *et al.* (2005) to describe the *Beggiatoa* metabolism (Table 7). This mechanism characterizes the “energy maintenance phase” of *Beggiatoa* filaments where the sulfide is completely oxidized to sulfate and the generated energy is sufficient for cellular activity (Sayama *et al.* 2005). In the model, we assumed that the rate of biomass increase due to bacterial growth is equal to its decrease due to cell death and endogenous metabolism including processes leading to a decrease in cell mass such as the oxidization of internal sulfur and nitrate for energy

purposes. Therefore, net biomass accumulation is zero and the volume of the cells remains constant during the simulation period.

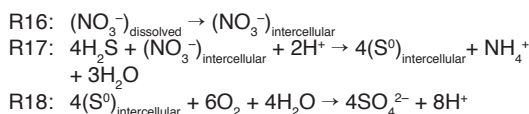
Although *Beggiatoa* filaments respire oxygen, their microaerophilic characteristic forces them to respond to high oxygen concentrations in the water (Møller *et al.* 1985). To cope with this inconsistency, these microorganisms adjust their vertical position in order to control the oxygen flux at the cell membrane. In highly oxic conditions, the filaments avoid high oxygen concentrations by converging below the DBL and forming a dense and smooth bacterial mat. When oxygen is limited under hypoxic conditions, the *Beggiatoa* community extends its filaments above the sediment surface to capture more oxygen (Jørgensen 1982, Møller *et al.* 1985). Under these conditions, the rougher surface sediment formed due to extended *Beggiatoa* filaments hinders flow in the viscous boundary layer and increases both the thickness of DBL (Jørgensen and Revsbech 1983) and the diffusion distance for substances from the water column to the sediment.

Møller *et al.* (1985) measured variations of 0.5 to 1.1 mm in DBL thickness over a *Beggiatoa* mat at high and low oxygen fluxes respectively under laboratory conditions. We used an average value of 0.8 mm in the model to calculate fluxes of different solutes across the DBL. Diffused oxygen and nitrate from the overlying water are exposed to a chemically active layer of *Beggiatoa* filaments while passing across the DBL (Fig. 2). We modified the upper boundary conditions for oxygen and nitrate by incorporating bacterial uptake rates into the mass conservation equations used for the derivation of sediment surface boundary conditions.

As a consequence of the *Beggiatoa* response to environmental variations, these microorganisms impose spatially fluctuating chemical changes to the sediment environment. These changes result in a spatial separation of oxic and sulfidic zones with 1–3 cm thickness by nitrate-storing *Beggiatoa* (Mußmann *et al.* 2003, Sayama *et al.* 2005, Kamp *et al.* 2006) or an overlap of oxygen and sulfide concentration profiles in micrometer scales when oxygen is the only available oxidant (Nelson *et al.* 1986). The model assumes a mature *Beggiatoa* community (i.e. the growth phase is passed) which uses both

Table 7. Chemical mechanism proposed by Sayama *et al.* (2005) to describe the *Beggiatoa* metabolism.

Stoichiometry of reaction



oxygen and nitrate for its metabolism and is able to store nitrate and extends its filaments to deeper sediment layers for capturing sulfide. Our modeled *Beggiatoa* culture inhabits the sediment surface layers down to the depth of 2 cm. We further assumed that the *Beggiatoa* position is steadfast during the simulation period.

Due to a spatial separation of the microbial matrix from the overlying turbulent water by the DBL, oxygen and nitrate transport from water to the *Beggiatoa* mat takes place by diffusion (Jørgensen and Revsbech 1983). Diffusion of substrates to the *Beggiatoa* surface membrane is a complex multidirectional transport of molecules. We simplified this complexity by incorporating uptake rates for the whole bacterial population into the reaction network of the sediment. We used the Monod-type kinetics to represent bacterial consumption rates of sulfide, oxygen and nitrate in the following model:

$$J_j = J_{env,j} \frac{C_j}{K_{af,j} + C_j} \quad (14)$$

where C_j is the extracellular concentration of substrate j (i.e. sulfide, oxygen, and nitrate), and $J_{env,j}$ is flux rate of substrate j across the *Beggiatoa* habitat. The Monod type function incorporates the limiting effects of ambient concentrations on uptake rates. The adjustable parameter of $K_{af,j}$ incorporates the limitations regarding binding affinity of the substrate j (Shuler and Kargi 2002). We assigned values of $K_{af,j}$ for different substrates in a way that the model produces overall substrate uptake rates comparable to experimentally measured values by other

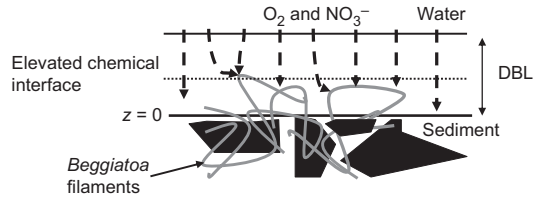


Fig. 2. Conceptualization of the elevated oxygen and nitrate chemical interface due to upward migration of *Beggiatoa* filaments under hypoxic conditions.

researchers (Table 8). The model assumes that both oxygen and nitrate fluxes in the top layers of the sediment and the sulfide production rate are the major environmental factors regulating the *Beggiatoa* metabolism. Hence, $J_{env,j}$ is equivalent to the fluxes of these substances in any given depth of the sediment occupied by *Beggiatoa* filaments corresponding to the maximum flux rates of substrates available for bacterial consumption. Taking into account the internal storage of nitrate for sulfide oxidization and sulfur for oxygen uptake, we assumed that the supply of these compounds does not limit the metabolic activities. Furthermore, the model treats *Beggiatoa* biomass as a non-limiting factor.

It is noteworthy that the *Beggiatoa* effects on the biogeochemistry of the sediments are highly dependent upon their density (Preisler *et al.* 2007). In the current model, we did not specify a density for the *Beggiatoa* community and assumed that both the distribution of *Beggiatoa* biomass and their chemical effects are uniform in their inhabited sediment and they are able to take up substrates with maximum rates equal to the fluxes

Table 8. Comparison of measured uptake rates of enriched *Beggiatoa* filaments by (Kamp *et al.* 2006) and modeled values.

Substrate	Uptake rate ($\mu\text{M day}^{-1}$)	Comment
Sulfide	514	After two days of experiment
Sulfide	186	After four days of experiment
Sulfide	194	Model
Oxygen	155	After two days of experiment
Oxygen	332	After four days of experiment
Oxygen	230	Model
Nitrate	257	Decrease in nitrate concentration after two days of experiment from initial value of $600 \mu\text{M}$ to $86 \mu\text{M}$
Nitrate	16	Decrease in nitrate concentration from $86 \mu\text{M}$ to $54 \mu\text{M}$ between day two and day four of experiment
Nitrate	26	Model

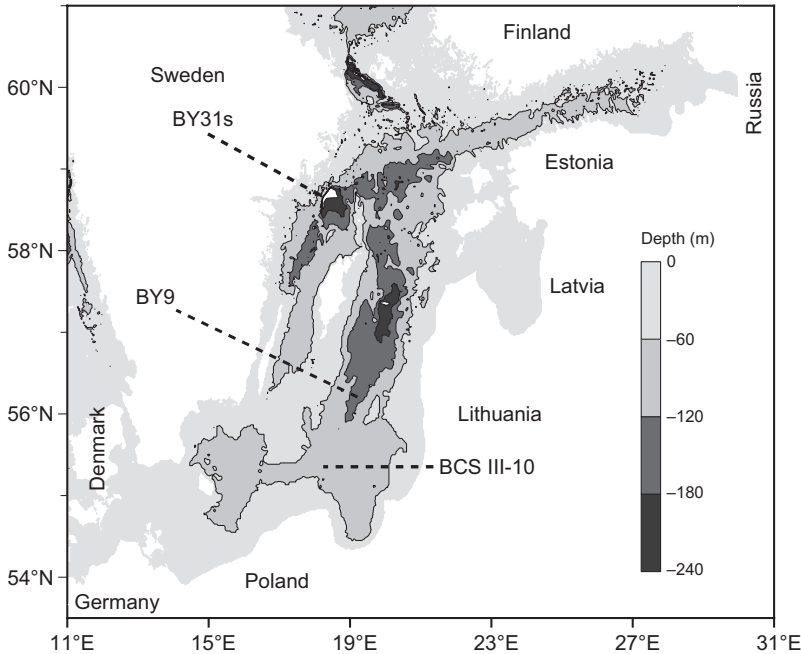


Fig. 3. Schematic map showing the location of sampling stations in the Baltic Sea by Carman and Rahm (1997). Bathymetric data is from Seifert and Kaiser (1995).

of substances across their habitat. For simplicity, we also assumed that the physical effects of these bacteria on the transport of solute and solid compounds are negligible in the modeled sediment. Furthermore, seasonal variations in the *Beggiatoa* density, the regulatory effects of sediment structure (Jørgensen 1977), and the role of other benthic microorganisms are examples of influential parameters on *Beggiatoa* metabolism which are not captured by the model. In this regard, the modeling experiment should not be considered a method for simulating the exact *Beggiatoa* behavior in natural sediments, but rather as a multi-variable approach for investigating their potential influences on sedimentary processes.

Results and discussion

Site description

Carman and Rahm (1997) analyzed surficial porewater composition from seven deep basins in the Baltic Sea. We considered three of the sites — BCS III-10, BY9, and BY31s — to be representative of hypoxic sediments (Fig. 3). These sites have water depths of 91, 123, and 125 meters, respectively. At the time of sampling, the

bottom-water oxygen concentrations were 82.5, 109.3, and 81.2 μM , respectively. BCS III-10 is located at the eastern end of the Stolpe Furrow. The topmost layer of the sediment was light brown in color and the lower layers were indistinctly laminated and contained “black striae”. BY9 is located at the southern end of the eastern Gotland basin. The upper 4 cm of the sediment was light brown and the pronounced lamination was observed in the sediment between the depths of 4 and 10 cm. BY31s is located at the edge of the Landsort Deep and the sediment from this station had brownish top layers and contained laminated layers with “black striae” down to the depth of 23 cm. The light brown color of the top layers of the sediments and the observed “black striae” suggest the presence of iron oxide and iron sulfide minerals, respectively (Carman and Rahm 1997).

The case of *Beggiatoa*-free sediment

Modeled concentration profiles of compounds as functions of sediment depth are presented in Fig. 4 together with measured porewater composition and organic matter contents from sediments of BCS III-10, BY9, and BY31s. We arbi-

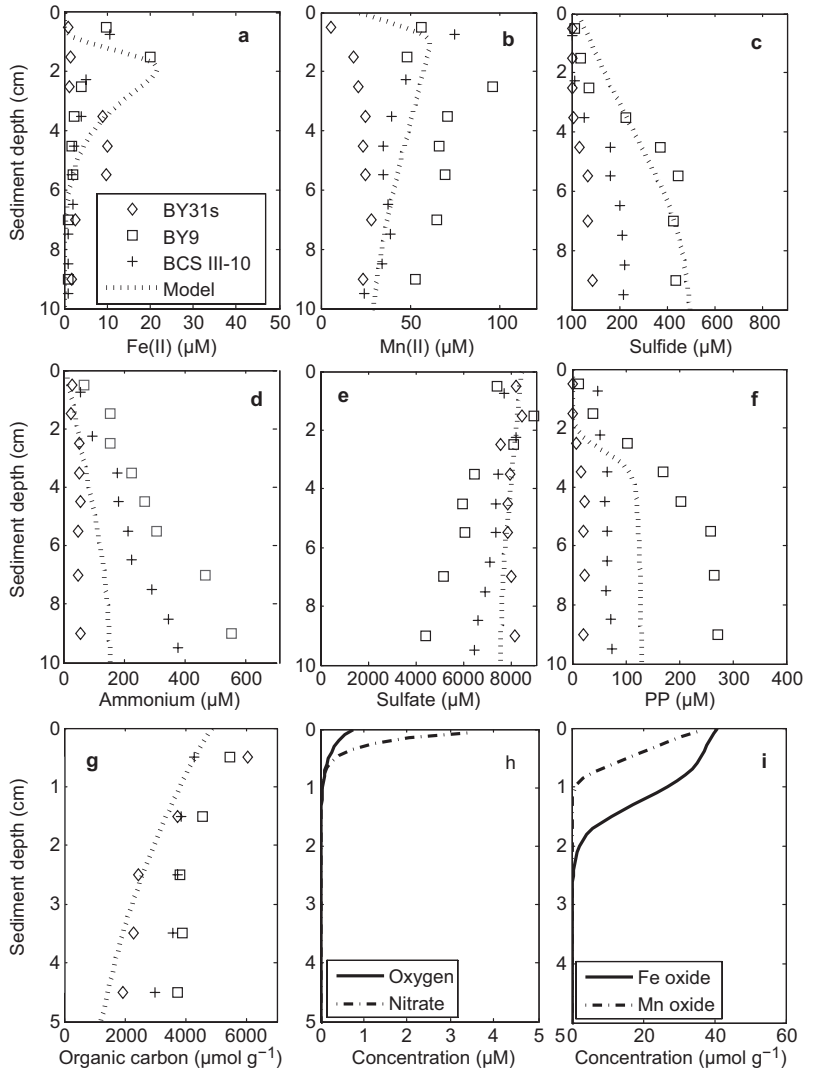


Fig. 4. Modeled and observed concentration profiles of sedimentary substances. **a–g:** comparison of the model results after four years simulation period (dashed lines) with three hypoxic sediment profiles, BCS III-10, BY 9, and BY 31s (Carman and Rahm, 1997). **h** and **i:** model results showing sequential depletion of oxygen, nitrate, Mn oxide, and Fe oxide through corresponding organic matter degradation pathways. Please note the different scales of the profiles of organic carbon, oxygen, nitrate, Fe oxide and Mn oxide.

trarily chose a simulation period of four years to calculate quasi-steady profiles of sedimentary compounds. It was not our intention to reproduce the observed data, but rather to provide a realistic representation of the sediment and pore-water profiles based on the dominant processes in the sediments. Simulated concentration profiles (dashed lines) reasonably correspond to the observed trends of porewater Fe²⁺ (Fig. 4a), Mn²⁺ (Fig. 4b), sulfide (Fig. 4c), ammonium (Fig. 4d), sulfate (Fig. 4e), PP (Fig. 4f) and the top layers' organic content (Fig. 4g) together with the sequential depletion of electron acceptors for organic carbon oxidization and the formation of suboxic and anoxic zones (Fig. 4h and i).

Simulated profiles of electron acceptors for organic carbon oxidization demonstrated that oxygen and nitrate (oxidants with the highest Gibb's free energy) were completely depleted in the upper 1 cm of the modeled sediment. A suboxic zone developed within the depth of 1 to 2 cm, where Mn and Fe oxides were terminal electron acceptors. Microbial reduction of these metal oxides resulted in a sharp increase in Fe²⁺ and Mn²⁺ concentrations, reaching their maximum levels in suboxic zones (Fig. 4a and b, respectively). Subsequent to iron oxide depletion, sulfate became the terminal electron acceptor and the organic matter degradation pathway shifted to sulfate reduction where the

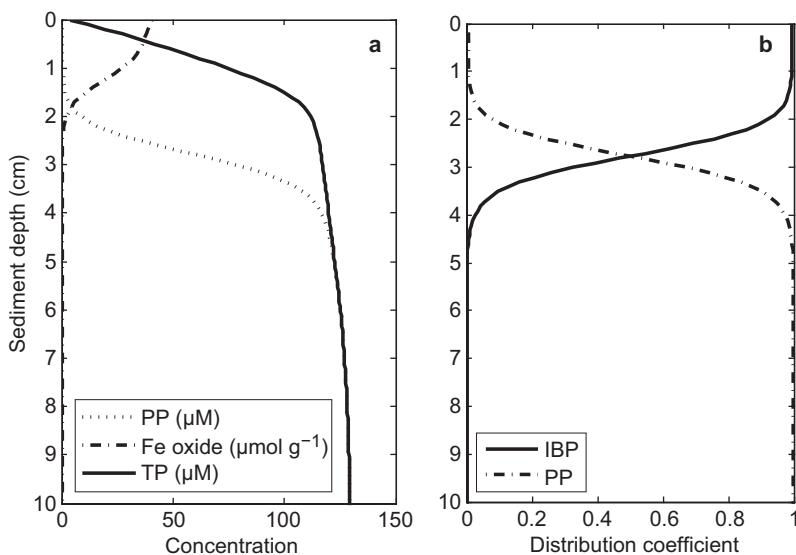


Fig. 5. Modeled concentration profiles of (a) PP, Fe oxides and TP; and (b) distribution coefficients of PP (λ_{PP}) and IBP (λ_{IBP}) as functions of sediment depth (Eqs. 9 and 10).

anoxic zone was developed. In this zone, below 3 cm, high rates of sulfate reduction resulted in extreme sulfide gradients and upward fluxes (Fig. 4c). It is noteworthy that the simulated profiles are the results of coupled organic and inorganic processes and represent their overall interactions.

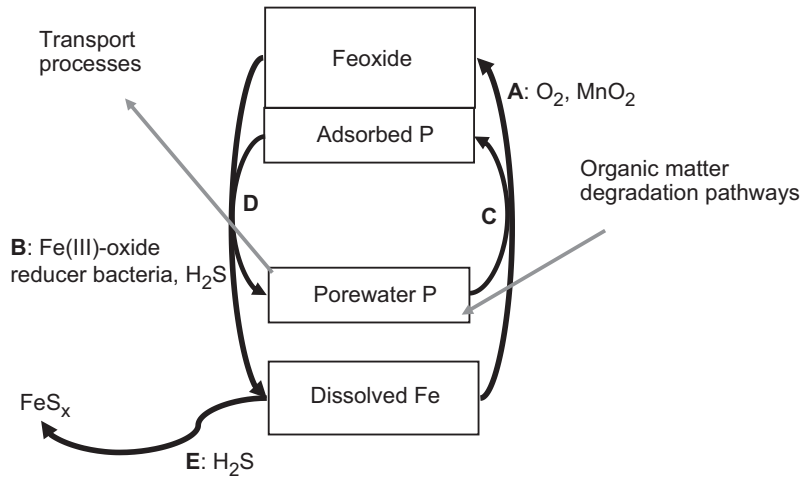
All pathways of organic matter degradation act as sources of phosphate in the sediments (Table 3: R1–R6). Simulation results showed an increase in TP contents (summation of IBP and PP) from the sediment–water interface down to lower depths (Fig. 5a). In the upper 1 cm of the modeled sediment, the distribution coefficient of IBP (λ_{IBP}) was equal to 1, indicating that in the presence of iron oxide minerals, the TP content of the modeled sediment was in iron-bound forms (Fig. 5a). Corresponding to the depletion of the pool of iron oxides in suboxic layers, λ_{IBP} decreased to 0 and λ_{PP} increased to 1, representing the transfer of phosphate from iron-bound forms to dissolved forms (Fig. 5b). These results imply that the transition from oxic ($\lambda_{\text{IBP}} = 1$) to suboxic ($0 < \lambda_{\text{IBP}} < 1$) and anoxic ($\lambda_{\text{IBP}} = 0$) conditions resulted in reductive dissolution of iron oxide minerals and mobilized phosphate in the modeled sediment environment.

The simulated concentration profile of iron oxides reflects the bioavailable portion of these minerals which are also active in the phosphate adsorption process. No data is available on iron

oxide contents of the sampled sediments to compare actual and calculated values. However, the availability of iron oxides was evident according to the observed light brown color in the upper layers of the sediments analyzed by Carman and Rahm (1997). The model simulated formation of iron sulfide with a depth integrated value of $33 \mu\text{mol g}^{-1}$ at the end of the simulation period. We assumed that deposition rate and initial concentration of these minerals were zero. Hence, the calculated concentration reflects iron sulfide minerals of authigenic origin. Although no quantitative measurements are available regarding iron sulfide concentrations in the sites, the “black striae” observed in the lower layers suggest the precipitation of these minerals in the hypoxic sediments of the Baltic Sea.

The results from investigations of the P retention processes in the sediments are presented as a simple conceptual model in Fig. 6. The figure depicts major processes and compounds controlling P mobilization in the sediments. Through oxidation of ferrous ions with oxygen and Mn oxides, sediment is enriched with Fe oxides (pathway A) and porewater P contents are partially or completely adsorbed on sorption sites of these minerals depending on the extent of the iron oxide precipitation process (pathway C). However, dissolution of Fe oxides to iron ions through chemical and microbial reduction (pathway B) releases iron-bound P in the sediment

Fig. 6. A conceptual model presenting major P retention processes in the sediments. (a) Fe oxide precipitation by oxygen and Mn oxide, (b) Fe oxide dissolution by Fe(III)-oxide reducer bacteria and sulfide, (c) P adsorption on Fe oxide minerals, (d) P desorption from Fe oxide minerals, (e) Fe sulfide precipitation.



(pathway D). Through the reaction of dissolved iron with hydrogen sulfide (pathway E) as a subsequent reaction to the chemical dissolution of iron oxide by sulfide (Rickard 1995), iron ions are converted into iron sulfide minerals resulting in the fixation of iron molecules in non-reactive forms regarding P adsorption.

To summarize, the conceptual model demonstrates that the mobilization (pathway D) and immobilization of P (pathway C) in the sediments are mainly regulated by the extent of the processes converting the iron supply of the sediment to reactive iron oxides or non-reactive iron sulfides, in terms of phosphate adsorption (pathways A, B and E). Similarly, field studies by other researchers demonstrated that the incorporation of iron ions into iron sulfide minerals considerably decreases the iron oxide formation and P retention in the sediments (Canfield 1989, Lehtoranta and Pitkänen 2003). Recall that the scheme in (Fig. 6) intends to specify the major processes and compounds controlling the mobility of P in the sediments of the Baltic Sea. Thus, we did not include less influential processes such as adsorption of P on other sedimentary minerals or the formation of P-containing compounds.

The case of *Beggiatoa*-covered sediment

In order to investigate the effects of *Beggiatoa* metabolism on the P retention processes, we hypothesized that the modeled sediment is cov-

ered by a *Beggiatoa* mat with the characteristics described above. All model properties were kept untouched and the uptake rates (Eq. 14) of sulfide, oxygen, and nitrate as well as *Beggiatoa* production rates of ammonium and sulfate were included in the sedimentary chemical network according to reactions R16 to R18 (Table 7). The model was then left for the same simulation period of four years as before to reach a quasi-steady state condition. The results are presented in Fig. 7, which includes model results from both *Beggiatoa*-free and *Beggiatoa*-inhabited sediments and demonstrate the changes in concentration profiles when the *Beggiatoa* metabolism is added to the sedimentary chemical network.

It turns out that the net impact of *Beggiatoa* interactions with sedimentary processes had no considerable influence on the PP concentration profile (Fig. 7a) of modeled sediment. However, in the presence of a *Beggiatoa* mat, the modeled sediment contained higher concentrations of Fe^{2+} and Fe oxide as compared with the *Beggiatoa*-free sediment (Fig. 7b and c). These differences between the two cases are attributable to *Beggiatoa* sulfide consumption (Fig. 7d). In the case of *Beggiatoa*-free sediment, sediment zones rich in iron oxides and iron ions (top sediment layers) are exposed to high concentrations of sulfide transferred upward from sulfidic layers and therefore the rates of Fe oxide dissolution and Fe^{2+} mineralization by sulfide (Table 5: R7 and R14, respectively) are high in upper sediment layers.

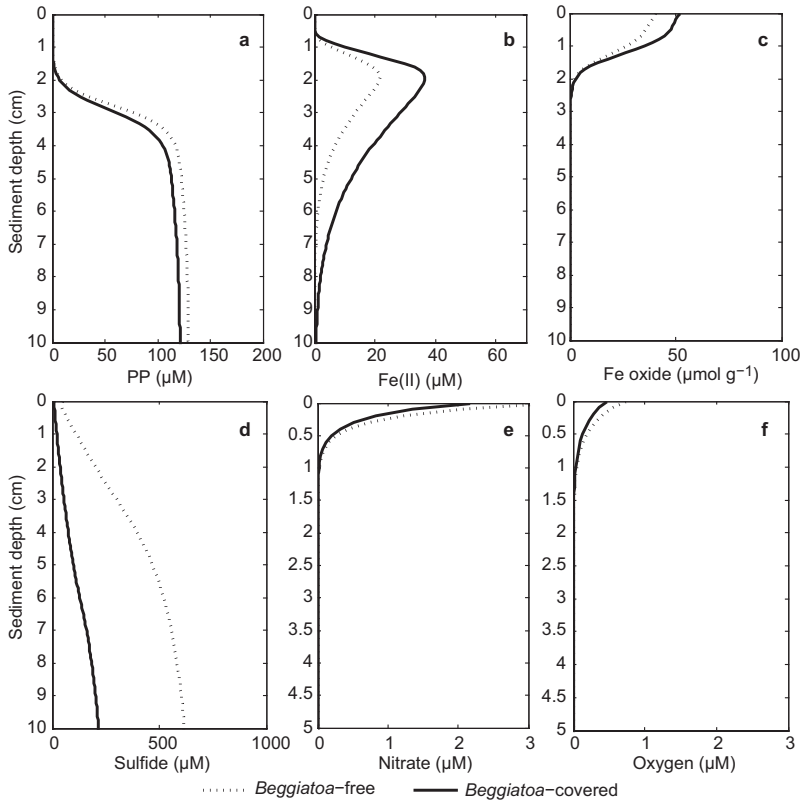


Fig. 7. Comparison of simulated concentration profiles of (a) PP, (b) Fe^{2+} , (c) Fe oxide, (d) sulfide, (e) nitrate, and (f) oxygen between the cases of *Beggiatoa*-free and *Beggiatoa*-covered sediments. Please note the different scales of the profiles of oxygen and nitrate.

The active iron oxide precipitation/dissolution cycle between oxic and anoxic layers of the sediment promotes the local scale P adsorption/desorption process (see Fig. 6). Contrary, iron oxide dissolution by sulfide and the following iron sulfide formation withdraw iron molecules from this cycle and decrease the supply of iron active in terms of phosphate adsorption. Chemical dissolution of iron oxides by sulfide and precipitation of iron sulfide in top sediment layers occur with lower rates in the presence of a *Beggiatoa* mat (Fig. 8). The model-calculated Fe:TP ratio (summation of Fe oxide and dissolved Fe^{2+} on molar basis and the TP ratio) of 6.2:1 for the upper 2 cm of the *Beggiatoa*-covered sediment. This value is 63% higher in comparison with the calculated Fe:TP ratio of 3.8:1 for *Beggiatoa*-free sediment under similar conditions. These results suggest that the separation of iron rich layers from the high concentrations of sulfide through *Beggiatoa* sulfide consumption increases the supply of iron available for the local scale P adsorption/desorption process

inside the sediment environment.

Nitrate and oxygen consumption by the *Beggiatoa* mat lowered the concentrations of these substances but did not inhibit their transport from the water to the uppermost sediment layers (Fig. 7e and f, respectively). Similarly, *in situ* measurements of nitrate and oxygen concentration profiles by other researchers demonstrated the transport of these compounds to the top layers of the sediments occupied by *Beggiatoa* mats (Mußmann *et al.* 2003, Preisler *et al.* 2007). A *Beggiatoa* community in complex and variable natural conditions might behave differently from the presented model. For instance, the model relies on the mechanism suggested by Sayama *et al.* (2005) for defining *Beggiatoa* substrate uptake. These researchers observed a complete shift from denitrification to “dissimilatory ammonium production” in the presence of *Beggiatoa* filaments. However, other studies suggested that *Beggiatoa* mats may perform denitrification rather than ammonium production (Sweerts *et al.* 1990). Hence, the role of *Beggiatoa*

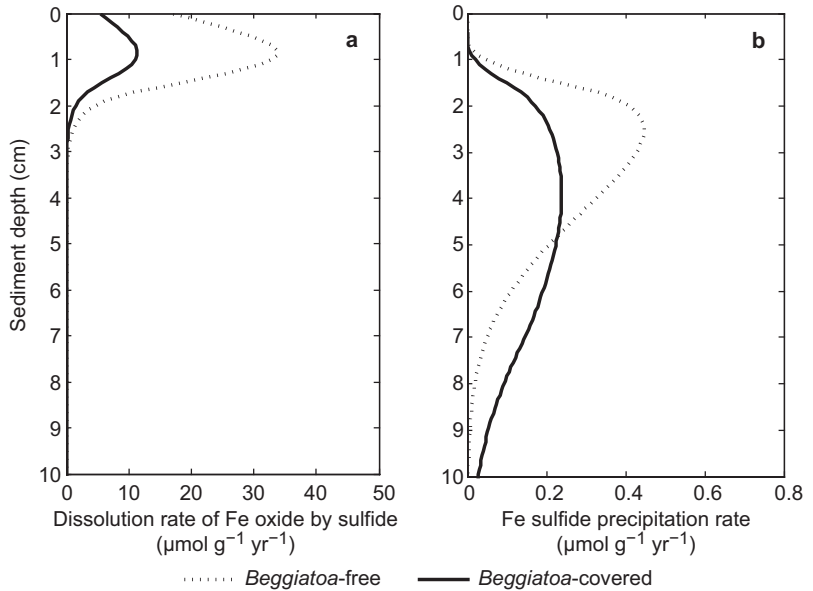


Fig. 8. Comparison of (a) dissolution rate of Fe oxide minerals by sulfide, and (b) Fe sulfide precipitation rate in the presence (solid lines) and absence (dashed lines) of *Beggiatoa* mat.

toa spp. in the N cycle in natural sediments might be different than what was predicted by the current model.

Furthermore, *Beggiatoa* mats on the sediments have a variety of densities which vary seasonally according to environmental conditions (e.g. Jørgensen 1977, Rosenberg and Diaz 1993). Biomass density is an important factor for the impacts of *Beggiatoa* mats on the sediments (Preisler *et al.* 2007). Although we did not specify the density of the *Beggiatoa* mat, bacterial biomass was treated as a non-limiting factor in uptake rates of the substrates representing the abundance of *Beggiatoa* filaments in the modeled microbial community corresponding to a microbial mat with a high biomass density. This assumption might lead to further overestimations of the impact of *Beggiatoa* when lacey cultures of these bacteria inhabit the sediment–water interface. The model did not specify sediment types and structure which are among other important factors on physiological behavior of *Beggiatoa* spp. in marine sediments (Jørgensen 1977). This simplification limits the applicability of the model when studying the *Beggiatoa* mats at different Baltic Sea areas with different sediment physical characteristics. However, the numerical experiment of this work was intended to study the potential influences of *Beggiatoa* mats on P retention processes. In this regard, the model

results demonstrated potential local scale interactions of sulfide-oxidizing *Beggiatoa* with the P retention processes in their inhabited sediments.

Implications for P management in the Baltic Sea

The amount of P released from newly formed anoxic/hypoxic sediments of the Baltic Sea can be more than the riverine P loads which makes P exchange across the sediment–water interface a critical process affecting both eutrophication and hypoxia in this marine system (Conley *et al.* 2009). About a third of the Baltic Proper bottoms were anoxic or hypoxic in the autumn 2008 (i.e. roughly all basins below 90 m, Hansson *et al.* 2008) and these conditions provide suitable habitat for the frequent occurrence of the genus *Beggiatoa*. The present model study highlighted the main processes regulating P retention in these sediments and demonstrated that *Beggiatoa* spp., as one of the most probable surface species on hypoxic bottoms (Rosenberg and Diaz 1993), potentially interact with these processes.

There is currently a great deal of research focused on remedy actions based on P retention in the sediments to deal with eutrophication in the Baltic Sea (e.g the Swedish “BOX project” and the Finnish “PROPPEN”). The P retention

capability of the sediment is limited when iron molecules are mineralized and buried as iron sulfides, but sulfide consumption by *Beggiatoa* mats is expected to have a positive contribution on P retention by increasing the supply of iron available for P adsorption/desorption in local scale hypoxic sediments. Furthermore, internal storage of nitrate by sulfide oxidizing *Beggiatoa* is about four orders of magnitude greater than ambient concentrations which make the widespread *Beggiatoa* filaments a potential sink for N in the Baltic Sea sediments (Rosenberg and Diaz 1993). Therefore, these bacteria may also play an important role in the regulation of the N stock in the Baltic Sea.

To the best of our knowledge, there is no comprehensive, large scale study focused on the spatiotemporal *Beggiatoa* distribution in the Baltic Sea. According to the presented results, we suggest that future remedy actions based on P retention in the sediments of the Baltic Sea should consider the role of *Beggiatoa* mats and its metabolism in sedimentary P retention processes. Information including detailed data on the spatiotemporal distribution of these microorganisms and their density as well as local scale measurements of biogeochemical parameters controlling *Beggiatoa* interactions with sedimentary processes is required in order to quantify the contribution of these bacteria to the biogeochemistry and retention of P on both local and basin scales. This information and environmental data will be useful for the management of present P in the Baltic Sea and future action planning.

Conclusions

Ongoing eutrophication builds up P storage in surficial sediments of the Baltic Sea comparable to almost a decade of riverine P load. It is well understood that shifts in bottom water conditions to hypoxia and anoxia result in both the mobilization of the IBP and the transfer of P to the overlying water body. The portion of hypoxic/anoxic sediments has increased with time in the Baltic Sea. These bottom conditions eliminate higher orders of life but make the new sediment surfaces suitable habitats for sulfide-oxidizing *Beggiatoa*. Previous studies by other researchers

provided information on *Beggiatoa* physiology and enzymology, and additionally suggested that these bacteria play an important role in the biogeochemistry of marine sediments.

In this work, we studied the effects of *Beggiatoa* metabolism on P retention using a diagenetic model based on the dominant processes controlling P mobility in the surficial sediments. In a comparison of the model results using the case of *Beggiatoa*-free sediment with available data, we showed that the model is able to simulate realistic vertical concentration profiles of incorporated compounds in the sediment-porewater medium. We also showed that both the mobilization and immobilization of P in the sediments are mainly regulated by the extent of iron oxide precipitation/dissolution and iron sulfide precipitation which induce the iron supply of the sediment to form reactive iron oxides or non-reactive iron sulfides in terms of phosphate adsorption.

In one scenario for *Beggiatoa*-covered sediment, we included the uptake rates of sulfide, oxygen, and nitrate, as well as production rates of ammonium and sulfate by the *Beggiatoa* mat in the chemical network of the modeled sediment. The results demonstrated that the interactions of microbially mediated redox reactions from the *Beggiatoa* metabolism with P retention processes potentially increases the supply of iron available for local scale P adsorption/desorption processes inside the sediment. This is done through the separation of iron rich layers from deeper layers rich in sulfide as the *Beggiatoa* filaments consume sulfide in the top layers of the sediment.

Finally, it seems that it would be beneficial in the future to increase the knowledge of the biogeochemistry of *Beggiatoa* spp. in marine systems in general and especially in the Baltic Sea where remedy actions based on P retention in the sediments are under assessment. Our current study is a point of departure for future investigations aiming to provide comprehensive information on the role of *Beggiatoa* spp. in the biogeochemistry of the Baltic Sea, through the integration of the modeling approach with field and laboratory measurements.

Acknowledgements: Part of this study was done in conjunction with the BOX-project and financed by the Swedish

Environmental Protection Agency. We are most grateful for the help offered by B.P. Boudreau regarding background information. We would also like to acknowledge the constructive comments from two anonymous referees of the article which helped to improve the manuscript.

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