

MODELLING PHOSPHORUS EXCHANGE AT THE SEDIMENT WATER INTERFACE OF A BRACKISH WATER BAY

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Key words: Phosphorus, sediment, early diagenesis, modelling.

Summary. Phosphorus plays a key role in the eutrophication of coastal waters. Despite this widespread agreement, its release mechanisms from the sediments (internal loading) still remain unclear. Phosphorus is present in the environment under various forms more or less refractory that can be classified as e.g. labile, organic phosphorus, redox-sensitive phosphorus and refractory. In northern Europe, the redox-sensitive part is significant and can play an important role in the release of phosphorus from the sediments. In this study, we presented our preliminary results on the modelling of phosphorus processes in the sediments of a small brackish bay of the Baltic Sea (Finland). The mechanisms controlling phosphorus concentrations in the sediments of the bay and the release of phosphorus to the water column were identified as redox-conditions and iron and sulphur chemistry. In this study, we presented a new modelling approach to link the phosphorus cycle to the oxygen, iron and sulphur cycles in the sediments. The new formulation allowed for the representation of the exchange processes between the sediments and the water concerning the three most reactive forms of phosphorus (dissolved, redox-sensitive and organic). The new model successfully simulated the profiles of phosphate, sulphate, iron ions, iron-bound phosphorus and ammonium concentrations in the sediments. Without the herein introduced reactions linking phosphorus to the iron and sulphur cycles, the model could not reproduce the low concentrations of phosphate in the top sediments.

1 INTRODUCTION

Phosphorus (P) is a key nutrient in primary production and, therefore, plays a major role in the eutrophication process, where excessive nutrient input enhances the development of phytoplankton. Although in coastal waters nitrogen is usually the limiting nutrient for algal growth, high concentration of phosphorus enhances the fixation of nitrogen from the atmosphere by Cyanobacteria¹. The phosphorus cycle in stagnant or slow moving aquatic ecosystems is dominated by the exchange of phosphorus between the sediments and the overlying waters². Phosphorus release from sediments is a complicated process having a major influence on coastal water quality³. Phosphorus is present in the environment under various forms more or less refractory that can be classified as, for example, labile P, organic P, redox-sensitive P and refractory P⁴. In northern Europe, the redox-sensitive part is

significant and can play an important role in the release of phosphorus from the sediments^{4,5,6,7}. The organic part is subject to a slow mineralisation process while the redox-sensitive part is subject to the fluctuation of organic matter, oxygen, iron and sulphate. The phosphorus exchange at the sediment-water interface is usually increased when the sediment surface becomes anoxic. This phenomenon can be explained by the reduction of ferric iron (Fe(OH)₃) to ferrous iron (Fe²⁺) that releases iron-bound phosphorus (redox-sensitive P)⁸. At present, few diagenetic models, representing mineralisation and processes (chemical and biological) affecting the sediments, deal with phosphorus and even fewer models with other forms than just dissolved phosphorus⁹. Phosphorus adsorption by the sediment is often dealt with an adsorption constant¹⁰. Since the beginning of the 1970's, fractionation methods of P in the sediments have been increasingly used to investigate sinks and sources of P generating new datasets for the modelling of phosphorus. In this study, we make a first attempt to model the reduction of the phosphorus retention capacity, deep in the sediments, by linking the P cycle to oxygen, iron and sulphur cycles in the sediments. The goal is to be able to model the quick changes in phosphorus release between oxic and anoxic conditions. Porewater and fractionation data from the Töölönlahti Bay in the Baltic Sea are used to validate the model.

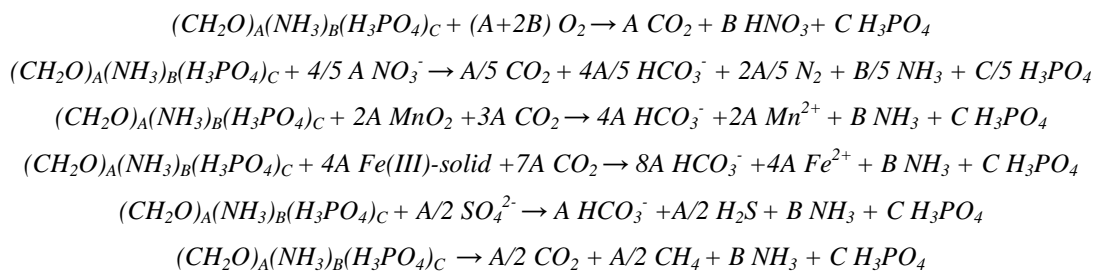
2 MODEL DEVELOPMENT

To model phosphorus exchange at the water-sediment interface we chose to build a new model using the CANDI (Carbon and nutrient diagenesis) model¹⁰ as a starting point. Mathematical models are an important tool in the study of early diagenetic processes as primary reactions (degradation of the organic matter) are coupled with a large number of secondary reactions (reoxydation, precipitation and adsorption of by-products).

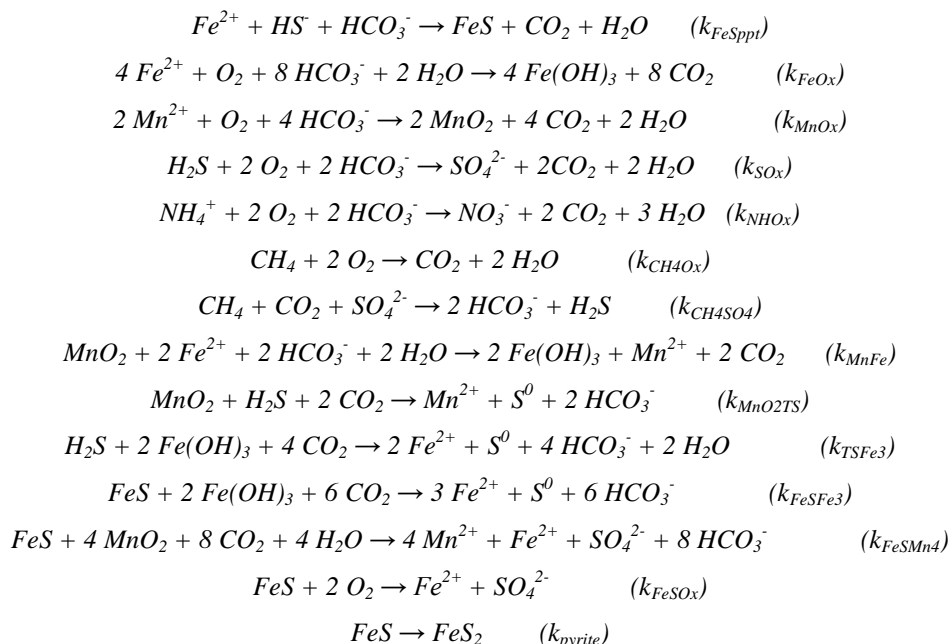
2.1 CANDI model

The CANDI model is a transport-reaction model for organic matter degradation and subsequent re-oxidation of by-products and the formation of iron sulphide (FeS) and pyrite (FeS₂). It is based on a set of General Diagenetic Equations (advection-diffusion-reaction)^{11,12}. Solutes included in the CANDI model are: oxygen (O₂), nitrate (NO₃⁻), ammonium (NH₄⁺), phosphate (PO₄³⁻), sulphate (SO₄²⁻), sulphide (H₂S), carbon dioxide (CO₂), methane (CH₄), manganese ion (Mn²⁺) and iron ion (Fe²⁺). Solid species include: organic carbon (Org-C) as three fractions of biodegradability, manganese (MnO₂-solid), iron (FeIII-solid) and FeS.

Primary redox reactions are (1):



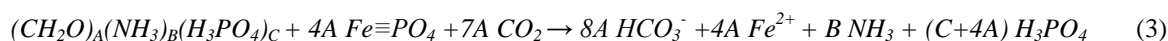
Secondary redox reactions are (2):



In the CANDI model phosphate is under a dissolved and an adsorbed form. Phosphate is produced during the degradation of the organic matter (1) and the adsorbed form is defined using an adsorption coefficient (K_{PA}). In the CANDI model, phosphate concentration in the sediment porewater depends on the phosphate concentration in the water column, transport processes (molecular diffusion, bioturbation, advection and irrigation), degradation of organic matter, and the adsorption coefficient. However, in this model there is no link between the phosphate concentration in the sediments and the aerobic/anaerobic conditions at the top of the sediment. Moreover, the reduction of ferric iron oxides deep in the sediments will not influence the phosphate adsorption coefficient in CANDI. These two phenomena are well documented in the literature⁷ and we intend to reproduce them here.

2.2 New phosphorus model

In this new approach we considered the formation of a solid phase species binding phosphorus onto hydrated iron oxides (iron-bound phosphorus: $Fe\equiv PO_4$) (4) that could be used as an oxidant terminal electron acceptor (TEA) for the degradation of the organic matter (3) or transformed into iron sulphide (5). The last two processes involved the release of phosphorus to the pore water. The new solid phase variable and the three additional equations were introduced into our model to connect phosphorus with the iron and sulphur cycles.



The proposed model represented the three most reactive forms of phosphorus in terms of exchange between the sediments and the water column: dissolved phosphorus (H_3PO_4), organic phosphorus ($((\text{CH}_2\text{O})_A(\text{NH}_3)_B(\text{H}_3\text{PO}_4)_C)$) and iron-bound phosphorus (redox-sensitive) ($\text{Fe}\equiv\text{PO}_4$). The adsorption constant (K_{PA}) from the CANDI model was removed. In the new model, phosphate bound to the sediments was no longer represented by an adsorption constant but rather as a reactive species ($\text{Fe}\equiv\text{PO}_4$) that could be dissociated by sulphide or used for the oxidation of the organic matter deep in the sediments. This new description allowed the differentiation of processes taking place in freshwater versus brackish and marine waters, where sulphate is present in the water column.

3 APPLICATION OF THE MODEL TO THE TÖÖLÖNLAHTI BAY

Töölönlahti Bay is located on the northern coast of the Gulf of Finland (Baltic Sea) and lies in the centre of the city of Helsinki (60°10'N, 24°56'E), capital of Finland (ca. 575,000 inhabitants). The bay is characterised as shallow with very eutrophic brackish water¹⁴. It is around 2 m deep and covers 20 ha. A detailed description of the bay and the data collected and presented in this paper can be found in Thouvenot-Korppoo et al. (submitted)⁷. The water in the bay is turbid throughout the year and substantial plankton biomass develops during the summer months¹⁵. Due to the shallowness of the bay and good mixing, oxygen levels remain acceptable in the water column. However, large amount of algae, settling to the bottom of the bay, cause oxygen concentrations to decrease close to the sediment surface¹⁶. Internal loading of phosphorus is recognised as the main problem delaying the recovery of the water quality after external loading was reduced¹⁴. Oxygen was identified as the main factor controlling the rapid release of phosphorus from the sediments to the water column, once depleted, and iron and sulphur cycles were suspected of directing the slow release of phosphorus to the water column even under good oxygen conditions⁷.

The model was run dynamically between spring and late summer, and the initial conditions were defined by the measurements taken during a sampling campaign in May 2007. Water quality data provided by the Environment Centre of the City of Helsinki were used as boundary conditions for the model over the period May to September. The results of the model were compared to the measurements analysed in September 2007.

Firstly, phosphate (Figure 1a), ammonium (Figure 1c) and iron sulphide (Figure 2a) concentrations were very low at the surface of the sediments before increasing with depth below a threshold located at a depth of 10 cm. Secondly, sulphate (Figure 1b) and iron-bound phosphorus (Figure 2a) were rather constant with depth before decreasing below the same threshold. Thirdly, iron ions (Figure 2b) formed a peak around the same threshold. These trends could be explained by the reduction of sulphate, used as an oxidant for the degradation of the organic matter, which produced sulphide, capable of precipitating iron ions. The precipitation of iron ions as iron sulphide prevented the recycling of iron ions into iron oxides that have the capacity to bind phosphorus⁸. The addition of the three new equations (3), (4)

and (5) to the model allowed the representation of the decreased capacity of the sediment to bind phosphorus deep in the sediments as was observed in the Töölönlahti sediments⁷.

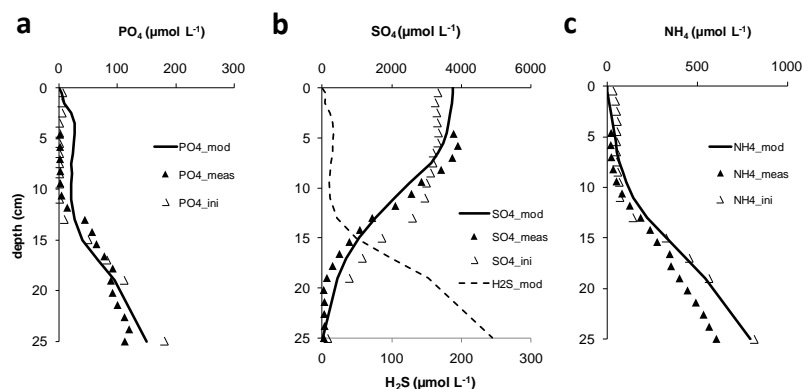


Figure 1: a) Phosphate (PO_4 , $\mu\text{mol L}^{-1}$), b) sulphate (SO_4 , $\mu\text{mol L}^{-1}$) and sulphide (H_2S , $\mu\text{mol L}^{-1}$) (dashed line) and c) ammonium (NH_4 , $\mu\text{mol L}^{-1}$) profiles in the sediments with initial conditions (open triangles), measurements (solid triangles) and results of the model (line).

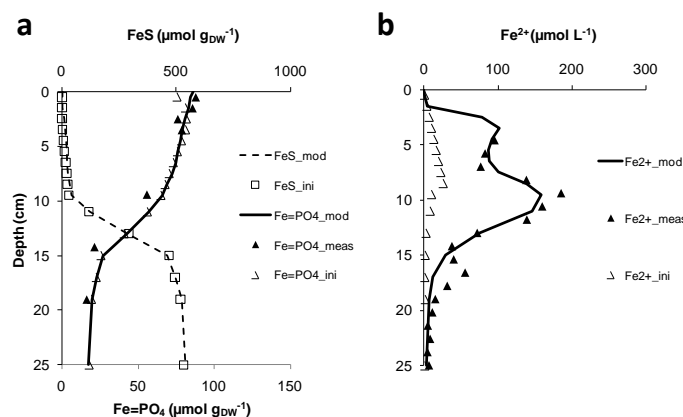


Figure 2: a) Iron bound phosphorus ($\text{Fe}=\text{PO}_4$, $\mu\text{mol g}_{\text{DW}}^{-1}$; triangles and solid line) and iron sulphide (FeS , $\mu\text{mol g}_{\text{DW}}^{-1}$; squares and dashed line) and b) iron ions (Fe^{2+} , $\mu\text{mol L}^{-1}$; triangles and solid line) profiles in the sediments with initial conditions (open markers), measurements (solid markers) and results of the model (line).

The coefficient of determination¹⁷ calculated for five variables (phosphate, ammonium, sulphate, iron ions and iron-bound phosphorus), as the mean of the five coefficients of determination, reached 0.91. The parameter values used to run the model are presented in Table 1.

The new reaction rate of k_{FePO_4} was low compare to, for example, the iron sulphide formation ($k_{\text{FeS}_{\text{ppt}}}$). However, the formation of iron-bound phosphorus represented an adsorption rather than a redox reaction between dissolved species. The slow formation of $\text{Fe}=\text{PO}_4$ could be explained by the competition of other ligands such as OH^- at $\text{pH} > 6.5$ (pH in Töölönlahti = 7). The reaction rate of $k_{\text{FePO}_4, \text{H}_2\text{S}}$ was higher than for example k_{TSFe_3} , which

represented the reaction of iron oxides with sulphide to form iron ions and sulphur. The rate k_{TSFe_3} was also low compared to the literature with a minimum described as 2×10^{-3} (^{18, 19, 20, 21}). This discrepancy could be explained by the use of total iron oxides instead of the distinction made in other models between reactive and refractory iron oxides. Therefore, the k_{TSFe_3} rate should be lower in our model and $k_{\text{FePO}_4, \text{H}_2\text{S}}$ higher if we considered that the entire total iron-bound phosphorus was reactive.

Table 1: Parameters included in the model with the description of the type of parameter considering the calibration process and their corresponding values.

| Parameter | Value | Range | Units | Type (I=independent or C=constrained) | References |
|---|--------------------|------------------------------------|----------------------------------|---------------------------------------|--------------------|
| Sedimentation: w | 0.6 | | cm yr ⁻¹ | I | 15 |
| Bioturbation: Db(0) | 6.7 | | cm ² yr ⁻¹ | I | 10, 20, 21 |
| Organic matter decay rate: k ₁ | 2×10^{-1} | 1×10^{-2} - 1.5 | yr ⁻¹ | C | 10 |
| Reaction rate: k _{MnOx} | 1×10^4 | $0 - 1 \times 10^4$ | mM ⁻¹ d ⁻¹ | C | 19, 20 |
| Reaction rate: k _{FeOx} | 3×10^2 | $1 - 2 \times 10^5$ | mM ⁻¹ d ⁻¹ | C | 20 |
| Reaction rate: k _{NHOx} | 5×10^1 | $10 - 2 \times 10^2$ | mM ⁻¹ d ⁻¹ | C | 10, 18, 19, 20 |
| Reaction rate: k _{SOx} | 2×10^1 | $4 \times 10^{-1} - 4 \times 10^3$ | mM ⁻¹ d ⁻¹ | C | 10, 18, 19, 20 |
| Reaction rate: k _{FeSOx} | 2×10^{-1} | $2 \times 10^{-1} - 6 \times 10^1$ | mM ⁻¹ d ⁻¹ | C | 10, 18, 19, 20 |
| Reaction rate: k _{CH4Ox} | 3×10^4 | | mM ⁻¹ d ⁻¹ | I | 10, 18, 19, 20 |
| Reaction rate: k _{CH4SO4} | 7×10^{-1} | $3 \times 10^{-2} - 3 \times 10^4$ | mM ⁻¹ d ⁻¹ | C | 10, 18, 19, 20 |
| Reaction rate: k _{MnFe} | 9 | $6 \times 10^{-3} - 3 \times 10^3$ | mM ⁻¹ d ⁻¹ | C | 10, 18, 19, 20, 21 |
| Reaction rate: k _{MnO2TS} | 3×10^2 | $1 \times 10^{-2} - 3 \times 10^2$ | mM ⁻¹ d ⁻¹ | C | 10, 18, 19, 20, 21 |
| Reaction rate: k _{TSFe3} | 1×10^{-5} | $1 \times 10^{-5} - 2$ | mM ⁻¹ d ⁻¹ | C | 10, 18, 19, 20, 21 |
| Reaction rate: k _{FeSFe3} | 0 | | mM ⁻¹ d ⁻¹ | I | 10 |
| Reaction rate: k _{FeSMn4} | 0 | | mM ⁻¹ d ⁻¹ | I | 10 |
| Reaction rate: k _{FeSpdt} | 1×10^2 | $0 - 3 \times 10^3$ | mM ⁻¹ d ⁻¹ | C | 10, 22 |
| Reaction rate: k _{Pvrite} | 1×10^{-4} | $0 - 3 \times 10^{-2}$ | d ⁻¹ | C | 10, 21 |
| Reaction rate: k _{FePO4} | 1×10^{-3} | $1 \times 10^{-3} - 1$ | mM ⁻¹ d ⁻¹ | C | |
| Reaction rate: k _{FePO4, H2S} | 2×10^{-2} | $1 \times 10^{-3} - 1 \times 10^1$ | mM ⁻¹ d ⁻¹ | C | |
| Irrigation rate: alpha | 1×10^{-1} | 0 - 1 | d ⁻¹ | C | 10, 18 |

To evaluate the benefit of adding the new reactions to an already rather complex model we ran the model without the new reactions and optimised it using the same variables as previously stated. This time, we could not reach the same optimised coefficient of determination (-0.28) and phosphate concentration in the sediment porewater increased below the sediment surface and was not kept at an undetectable level down to a depth of 10 cm. Therefore, the addition of new equations to the model was beneficial for the modelling of phosphate concentration profiles and the description of phosphorus processes in the sediments of the bay.

4 CONCLUSION

The goal of this modelling work was to develop a predictive capability for the transitions of phosphorus fractions (particulate, organic, inorganic) and their effects on the water quality.

The presented dynamic model of early diagenesis was used to compute the interaction between 23 biogeochemical reactions. The new model represented the cycling of carbon, phosphorus, nitrogen, manganese, iron, and sulphur in brackish and marine sediments. The introduction of three new equations (3, 4 and 5) and one new variable (iron-bound phosphorus) to a previous model allowed the representation of the loss in the capacity of the sediment to bind phosphorus caused by the precipitation of iron as iron sulphide. These three reactions enabled to model the increase of the phosphorus concentration deep in the sediments as observed in the Töölönlahti case. The model successfully simulated the concentration profiles of phosphate, sulphate, iron ions, iron-bound phosphorus and ammonium. As a next step, the model needs to be tested in regard to the exchange of phosphorus at the sediment-water interface under aerobic versus anaerobic conditions at the surface of the sediments. Furthermore, a comprehensive sensitivity analysis will be performed to identify the key reactions taking place in the Töölönlahti sediments (e.g. organic matter decay rates, irrigation and bioturbation processes) as well as to investigate the sensitivity of the results to the initial conditions in the sediments.

ACKNOWLEDGEMENTS

This study was based on a cooperation between the Helsinki University of Technology and the Finnish Institute of Marine Research. It was funded by Maa ja Vesitekniikan Tuki Ry. The experiments in the Töölönlahti Bay were carried out with the help of the City of Helsinki Environmental Centre.

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