

### Use of phosphorus fractionation data for modelling phosphorus exchange at the sediment water interface of coastal water systems

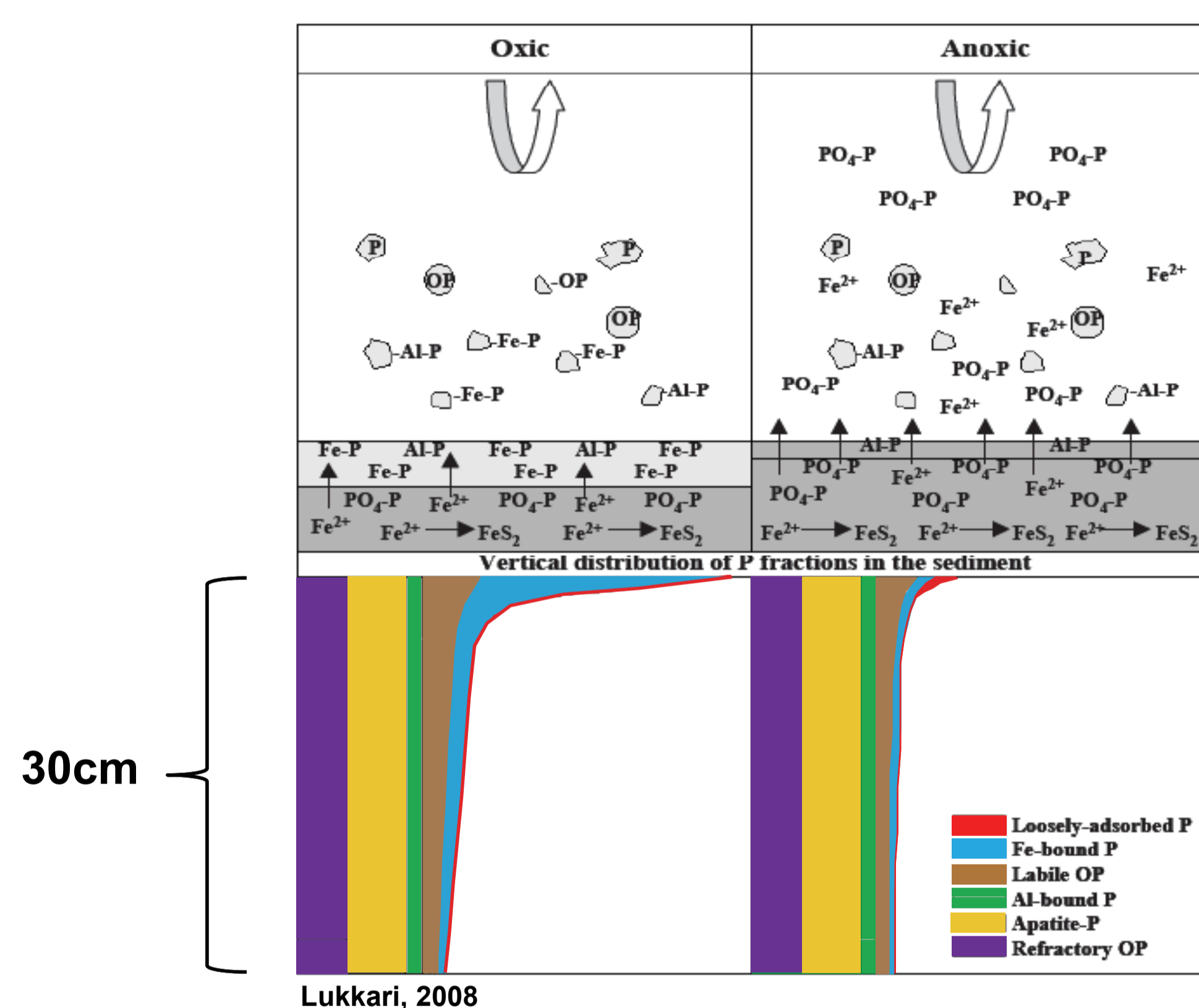
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## I. P in coastal waters

Phosphorus (P) is a key nutrient in the eutrophication process of coastal waters, which enhances the growth of Cyanobacteria. In slow moving aquatic ecosystems, the phosphorus cycle is dominated by the exchange of phosphorus between the sediments and the overlying waters.

In the sediments, P is present under various, more or less refractory, chemical forms that can be classified as e.g.:

- labile or loosely adsorbed P
- redox-sensitive (iron-bound) P
- reactive organic P
- P bound to aluminium oxides
- apatite P
- refractory organic P



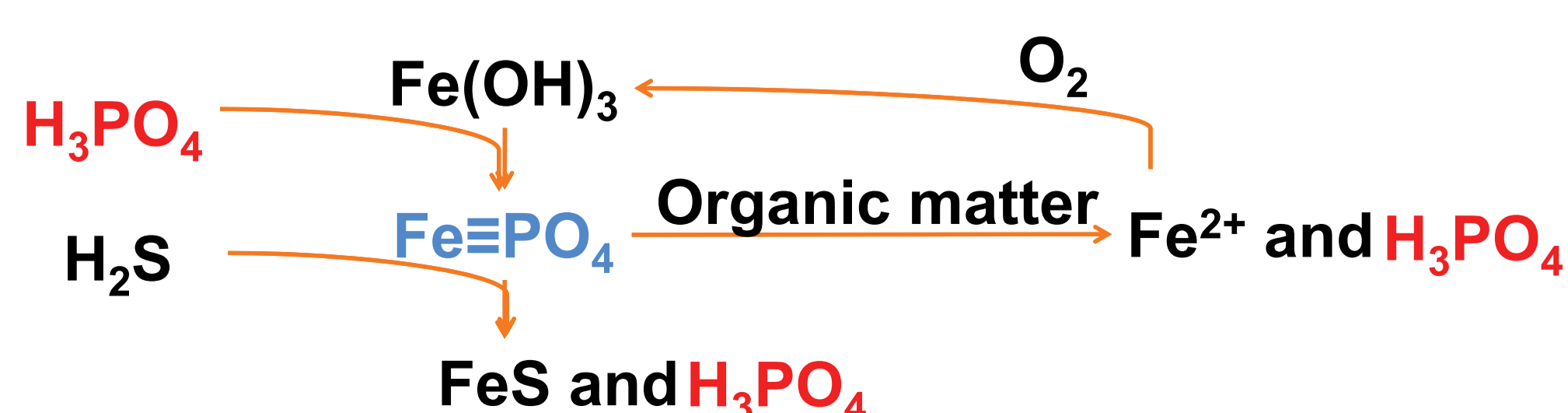
Example of possible chemical forms of phosphorus in the sediments under oxic or anoxic conditions in the water column.

## II. Mathematical model

Each of the P forms reacts differently to changing conditions in the environment. We conducted field investigations in a brackish water bay of the Baltic Sea and identified bio-irrigation, redox-conditions and iron and sulphur chemistry as the key factors controlling phosphorus concentrations in the sediments and the release of phosphorus to the water column. We developed an early diagenetic model based on CANDI (Boudreau, 1996) that represents the cycling of carbon, nitrogen, manganese, iron, and sulphur and the three most reactive forms of phosphorus (dissolved, redox-sensitive and organic). In this new approach, we were able to link the phosphorus cycle to the oxygen concentration and iron and sulphur cycles in the sediments. This addition enabled us to represent the loss in the capacity of the sediment to bind phosphorus caused by the precipitation of iron as iron sulphide.

3 new equations added to the diagenetic model:

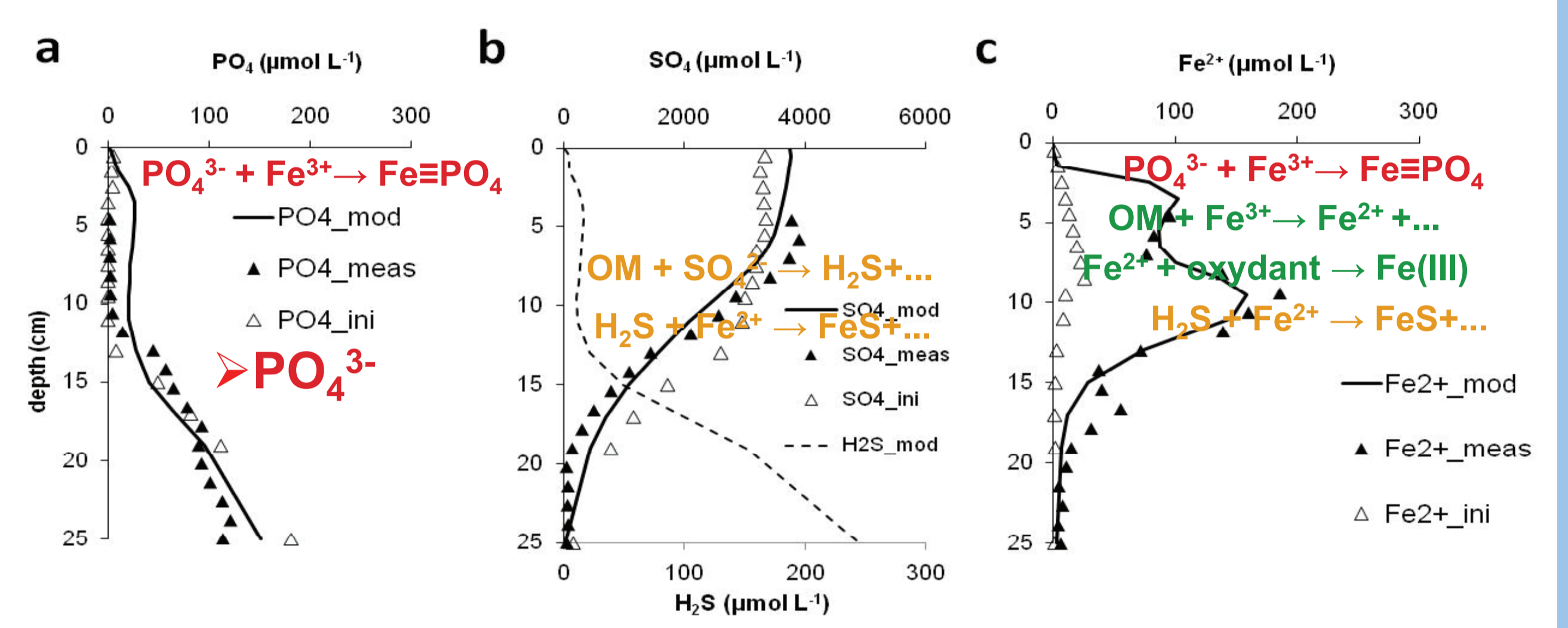
- $Fe(OH)_3 + H_3PO_4 \rightarrow Fe\equiv PO_4 + 3H_2O$  ( $k_{FePO_4}$ )
- $Fe\equiv PO_4 + H_2S \rightarrow FeS + H_3PO_4$  ( $k_{FePO_4, H_2S}$ )
- $(CH_2O)_A(NH_3)_B(H_3PO_4)_C + 4A Fe\equiv PO_4 + 7A CO_2 \rightarrow 8A HCO_3^- + 4A Fe^{2+} + B NH_3 + (C+4A) H_3PO_4$



## III. Results

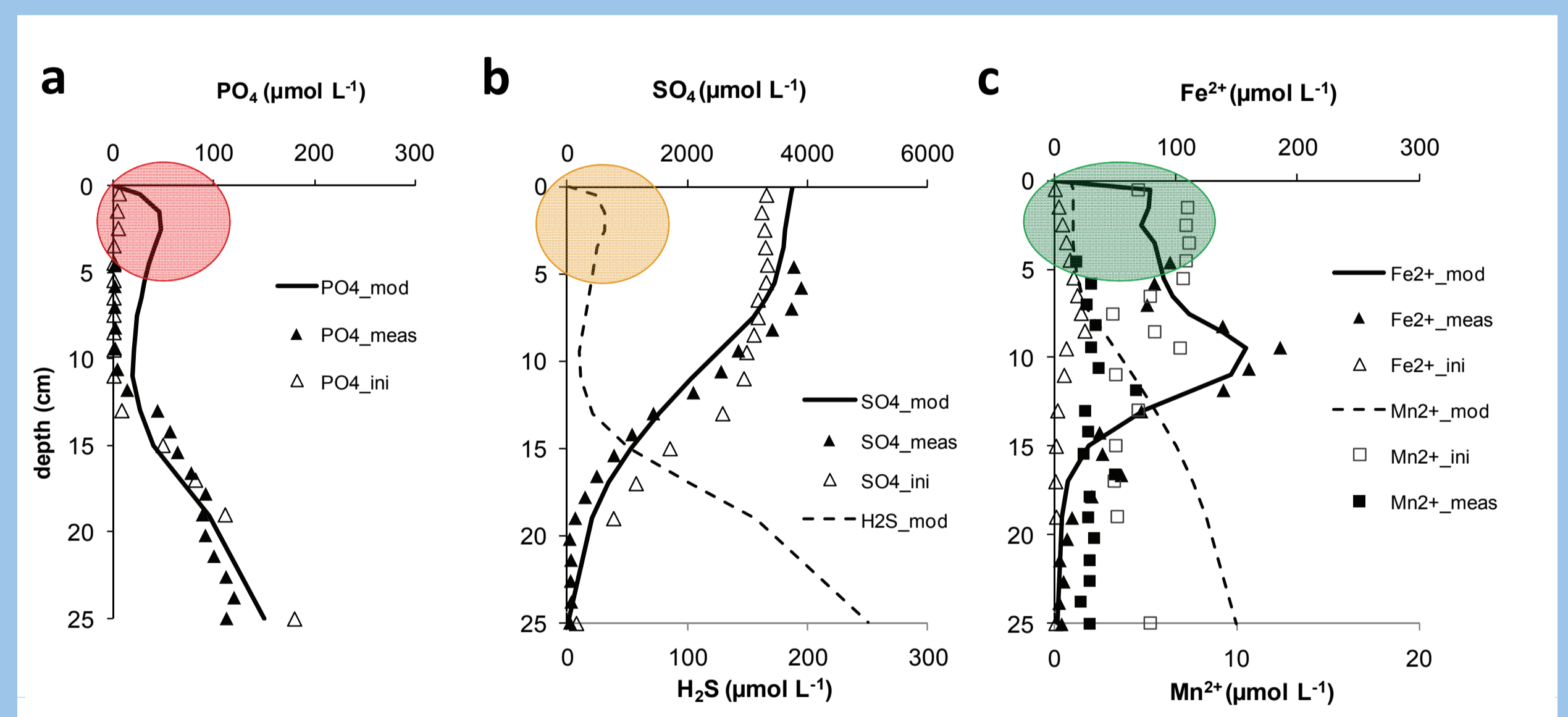
### 1) Profiles

The model successfully simulated the profiles of phosphate, sulphate, dissolved iron, iron-bound phosphorus (redox-sensitive P) and ammonium concentrations in the sediments. The coefficient of determination calculated as the mean of the five coefficients of determination, reached 0.91.



### 2) Fluxes

Fluxes at the sediment-water interface were greatly increased under anoxic conditions (160  $\mu\text{mol P m}^{-2} \text{d}^{-1}$ ) compared to oxic conditions (30  $\mu\text{mol P m}^{-2} \text{d}^{-1}$ ) at the sediment surface.



## IV. Conclusion

The introduction of three new equations 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. The model successfully simulated the concentration profiles of phosphate, sulphate, dissolved iron, iron-bound phosphorus and ammonium. Moreover, phosphorus fluxes at the sediment-water interface were well represented and greatly increased under anoxic conditions compared to oxic conditions at the sediment surface. Further work includes, a comprehensive sensitivity analysis to identify the key reactions taking place in the sediments of the bay (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.

### References:

- > M. Thouvenot-Korppoo, K. Lukkari, J. Järvelä, M. Leivuori, T. Karvonen and T. Stipa, "Phosphorus release and sediment geochemistry in a brackish water bay of the Baltic Sea" (under review).
- > K. Lukkari, 2008. "Chemical characteristics and behaviour of sediment phosphorus in the Northeastern Baltic Sea", Academic dissertation at University of Helsinki, Finland.
- > B.P. Boudreau, 1996. "A method-of-lines code for carbon and nutrient diagenesis in aquatic sediments", *Computers & Geosciences*, 22(5): 479-496.