

Response to reviewer #1

Overall Quality of the Paper:

This paper makes important contributions to understanding the main drivers of phosphorus burial in coastal sediments, which should be of interest to readers of Biogeosciences. A major finding of this paper is the potential importance of vivianite in the burial of P in estuarine sediments. The paper reports the identification of vivianite crystals in one core sample and presents a model of drivers of P burial that suggests that vivianite may account for about 40% of the P burial at that sample site. The paper also presents a model predicting that vivianite burial increases as salinity decreases and deposition of iron decreases. Therefore, increases in river flow and riverine iron input clearly have the potential to increase phosphorus burial.

Reply: We thank the anonymous referee for the positive remarks and insightful comments. Below, we reply to all of the comments and we indicate where and how we revised the manuscript.

Scientific Questions and Issues:

Title and Abstract:

Comment #1:

The title: "Variations in river input of iron impact sedimentary phosphorus burial..." is a bit misleading. I suggest that the authors change the title so that it does not imply that the study directly linked changes in river input of iron to changes in P burial. No measurements of riverine iron inputs are presented.

Reply: We agree with the reviewer that measurements of riverine Fe input would form a useful addition. Unfortunately, long term measurements of total Fe input are not available for the Ore River (or any other rivers in the region) and therefore cannot be included in our manuscript. However, by modelling key porewater and solid phase depth profiles in the Ore Estuary, we demonstrate that large temporal changes in Fe and organic matter input are necessary to fit our model to the measured data at this site (section 3.4). Because this is such an oligotrophic coastal region, the large temporal changes in Fe and organic matter input to sediments located at a river mouth can only be explained by variations in river input. We will, however, change the title to: "Variations in iron input impact sedimentary phosphorus burial in an oligotrophic Baltic Sea estuary".

Comment #2:

Data on water flow for the Ore River and other Swedish Rivers are presented but it is not entirely clear that profiles of iron and phosphorus in the sediment correlate with periods of high water flow. Two peaks in total Fe concentration in the sediment are evident at depths where sediment was apparently deposited during years preceded by years of low flow in the Ore River but the flow during the years of deposition was not exceptionally high compared to other years (Fig. 2).

Reply: We agree that the river flow in the years after each relatively dry period (1976 and 1996) was not exceptionally high. The mechanisms that we propose in this manuscript as a reason for the enhanced input of Fe depend on the relatively low river flow in the years 1976 and 1996 being followed by a higher flow when directly compared to the preceding dry period. For clarity we changed the text:

P2. Line 25 from "In ensuing wet periods" to "After dry periods"

P.13 S.5 from "In the following wet years," to "in the following years".

P14 S.14 from "in a wet period directly following a dry period on land in 1976 and 1996," to "in a period following a dry year on land in 1976 and 1996"

Comment #3:

The pattern of flow rate for 86 Swedish Rivers combined (Fig. S.8) is somewhat different from that of the Ore River.

Reply: Spatial and temporal patterns of rainfall over Sweden are expected to differ and result in differences in river discharge between the 86 rivers and the Ore River. Meltwater, for example, plays a more important role for rivers at high latitudes when compared to lower latitudes. As described on P.13 in lines 4-11, the 1996 dry period affected the whole Baltic Sea. This was less so for 1976.

Comment #4:

Finally, a lack of salinity gradient among the sample sites related to their distance from the mouth of the Ore River makes it unclear that discharges of iron from the Ore River would reach the sample sites.

Reply: All sample sites are not far from the river mouth, which is indicated with a star in Figure 1A. There is no salinity gradient in the bottom water of this salt wedge estuary. The particle plume from the river varies with time and is known to reach all of our sample sites (Malmgren & Brydsten, 1992).

We now mention this in section 2.1 (Lines 18-19): “While surface water salinity varies with time and distance from the river, there is no salinity gradient in the bottom water of this estuary. The spatial extent of the particle plume from the river varies with time but is known to reach all of our sample sites (Malmgren & Brydsten, 1992). “

Comment #5:

Similarly, lines 10-11 in the abstract are misleading because riverine inputs of iron and organic matter were not measured. Moreover, the claimed increase in river flow is not clear from the data, which mainly show distinct years of low flow preceding the timing of evident enrichments in iron and sulfur. Otherwise, the abstract is clear and reflects the findings of the study.

Reply: See reply to comment #1 and #2. We have modified the text (lines 10-11) to clarify that input of Fe and organic matter is enhanced after dry periods: “Distinct enrichments in sediment Fe and sulfur at depth in the sediment are attributed to short periods of enhanced input of riverine Fe and organic matter. These periods of enhanced input are linked to variations in rainfall on land and follow dry periods.”

Comment #6:

Section 2.3: Potential for vivianite extraction

This study used a serial extraction method (SEDEX) to characterize five forms of particulate P in sediments (Ruttenburg 1992 modified by Slomp et al. 1996, see p. 5 lines 24-33). One of those extractions uses citrate-dithionite-bicarbonate (CDB) to extract P bound to iron oxides, with the dithionite reducing Fe³⁺ to Fe²⁺. The authors mention that CDB also extracts vivianite, citing two references for this (p. 5, Line 26). Similarly, Hartzell et al. 2017 (cited on p.2 line 35) suggested that the P extracted with CDB might be mainly from vivianite in samples where Fe²⁺ was abundant and no Fe³⁺ could be detected. This makes me wonder whether SEDEX could be modified to estimate vivianite concentration separately from iron oxide bound P by preceding the CDB extraction with an extraction using just citrate-bicarbonate. Omitting the dithionite might make this extraction specific to P bound to Fe²⁺, as in vivianite. Having a serial extraction to estimate vivianite concentrations would be very helpful for evaluating the importance of vivianite in P burial. Would the authors comment on this idea?

Reply: We are citing Dijkstra et al. (2014) and Nembrini et al. (1983) here because they demonstrated that vivianite is extracted in the CDB step of the SEDEX method. We agree with the reviewer that an extra step, which would be specific for vivianite, would be helpful to get a better handle on the importance of vivianite in sediments. We are, however, not aware of a suitable, well tested step specific for vivianite. We did not test any other extraction methods, such as a CDB step without dithionite, to extract only vivianite. Therefore, we cannot comment on this idea.

Comment #7:

Section 3.1: Why just model NB8? Model other cores too? How representative is NB8?

Reply: In this study we wished to assess the burial of P in and below the SMTZ and the factors contributing to temporal variations in P burial, including the role of the rate of sedimentation. As we were not able to sample below the SMTZ at sites NB1, N6 and N10 (April) and the geochemistry of sites N7 and NB8 is comparable, we focused on site NB8. At site NB8 we subsequently performed three types of chemical extractions and experimental work to allow for visual observations of vivianite. We did not obtain these data for the other sites. The geochemistry at site NB8 is strikingly similar to that at another site with a high sedimentation rate in the Bothnian Sea (Egger et al., 2015a, b), as is discussed in the manuscript (e.g. p2, lines 15-17).

We have changed the text in the model description section to clarify that we selected NB8 because it has a shallow SMTZ and a relatively high sedimentation rate (P.7 line 3-4): "Site NB8 was characterized by a SMTZ close to the sediment-water interface and a relatively high sedimentation rate (Table 1)."

Comment #8:

On p. 7, Lines 3-4, the authors state that "a reactive transport model was applied to key porewater and solid phase depth profiles for site NB8." Does this mean that the field data to parameterize the model came only from site NB8? This should be clarified on p. 7 line 15.

Reply comment #9:

Reply: We now explicitly mention site NB8 in this sentence: "The model was parameterized using data site NB8,"

Comment #9:

Also it would be good to explain why the model was not applied for other sites as well as NB8.

Reply: See reply to comment #7.

Comment #10:

Data points for the other sites plotted on the graph vs. sedimentation rate on Fig. 9A suggest that the model was applied to the other sites, at least partly. Site NB8 is especially interesting because the high rate of sedimentation there suggests a high rate of P burial. How typical are conditions at site NB8? It would be good to address this question somewhere in the paper.

Reply: We indicated in the caption that these are measurements. We now also included this in the figure itself. Regarding the representativeness of NB8: see reply to comment #7.

Comment #11:

Section 3.4: Why would Fe:P decline with increasing riverine input of Fe? p. 8 Line 26-27: Why was it assumed that Fe:P would decline if riverine Fe input increased? It seems possible that riverine input of P in eroded soils or suspended riverine sediments might be tightly coupled with riverine input of Fe due to the chemical association of Fe and P in the soils or sediments. Increased river flow might increase particle transport without changing Fe:P. It is interesting to explore the implication of varying the Fe:P ratio either up or down but the authors should explain why increases in particulate Fe input would not be accompanied by similar increases in particulate P input. One possibility, implied later in the paper, is that the Fe transport is associated more with organic carbon than with suspended soils or sediments.

Reply: We agree with the reviewer that enhanced input of Fe could lead to enhanced input of P in agricultural environments where reactive P is abundantly present. However, as the area around the northern Baltic Sea consists mainly of natural and not agricultural land, changes in the Fe:P ratio are expected to occur when concentrations of Fe strongly increase. Moreover, we were not able to model the key porewater and solid phase depth profiles when assuming an invariant Fe:P ratio.

We have now added text on page 8 to explain this (line 27): "This assumption is based on the dominance of natural forest and wetlands in the region (Björkvald et al., 2008). We note that the model results were very sensitive to the P:Fe ratio and that we could not model the key profiles when assuming a higher P:Fe ratio".

Comment #12:

Sections 5.1 - 5.3: The parallels of FeOx and Fe-P in NB8 core might suggest that the buried Fe-P is bound to FeOx. The profile of FeOx parallels that of Fe-P in core NB8 (Fig. 6) suggesting that Fe-P concentration may be closely tied to the FeOx concentration. Despite this, the model suggests that the Fe-P becomes increasingly associated with Fe²⁺ as depth increases below the SMTZ. This seems a bit puzzling. Does the ratio of FeOx to Fe-P increase with depth? The profiles in Fig. 6 suggest that there might be enough FeOx below the SMTZ to bind the Fe-P. Is the deep FeOx not an effective P sink for some reason? Does FeOx bound P switch to Fe²⁺ bound P (vivianite) below the SMTZ while FeOx persists or increases in concentration?

Reply: We agree with the reviewer that there are strong parallels between the FeOx and Fe-P profile at site NB8. However, these parallels are mainly found in and above the SMTZ where vivianite plays a minor role. Below the SMTZ, FeOx slightly declines with depth, whereas Fe-P concentrations are variable. We realize that our terminology could be misunderstood here given that the extraction steps for Fe-oxides (Fe ox) could also extract Fe from vivianite. We have now changed Figure 6 and its caption and our method section to convey that vivianite Fe is also extracted in the HCl and CDB steps (p5, lines 11-13).

There is indeed a sink switch between Fe oxide bound P and Fe(II)-P minerals below the SMTZ. This is explained in the introduction (p2, lines 12-17) and is also discussed in great detail by Egger et al. (2015a). For clarity, we have now added text in section 5.1 briefly explaining the source of the Fe²⁺ and phosphate in the porewater: "As discussed in detail by Egger et al. (2015a), vivianite formation is generally most pronounced in sediments below the SMTZ, where both Fe²⁺ and HPO₄²⁻ accumulate in the porewater due to dissolution of Fe-oxides and release of associated P".

We have now also added a figure showing this relative distribution, both for Fe and P, as calculated with the model (Fig. S.7) and corresponding text in the results (p10, line 29): "At depth, P bound to vivianite becomes more important compared to P bound to Fe oxides (Fig. S.7)."

The relative contribution of Fe-oxide bound P and vivianite is discussed in lines 9-11 on page 12. “Due to dissolution of Fe oxides and vivianite formation in the sediment the fraction of P bound to vivianite increases with depth (Fig. S.7).”

Comment #13:

Alternatively, does organic Fe convert to vivianite Fe below the SMTZ?

Reply: All Fe species which can be mobilized to the pore water potentially contribute to the formation of vivianite. In the applied Fe extraction we did not include a step, which is specific for organic Fe. However, labile organic Fe complexes are expected to be extracted in both Na-acetate and hydroxyl-HCl (step 1 and step 2; Jilbert et al., 2018). This labile organic Fe fraction is expected to be small.

Comment #14:

To understand the change in P partitioning with depth at NB8, I think it would be helpful to see the observed profiles of total Fe (Fig. 5), FeOx and Fe-P (Fig. 6) together in the same figure. Also in the same figure, it would be good to include the profiles of vivianite P and Fe oxide bound P as inferred from the model. It would also be interesting to illustrate how much of the CDB extracted P (referred to as Fe-P) was associated with Fe³⁺ vs. Fe²⁺ concentrations at site NB8 predicted by the model. This might help assess whether CDB extracts might be useful for quantifying vivianite. Does the sum of FeOx-P and vivianite P equal the Fe-P as measured in the CDB extract? Is there some additional P extracted by CDB or is the sum of FeOx-P and vivianite-P larger than CDB extractable P?

Reply: Since the HCl and CDB-extractable Fe is only a relatively small proportion of the total Fe and includes Fe in both vivianite and Fe-oxides (see reply to comment #12), we do not see what can be gained from repeating the total Fe profile in Fig. 6. We do agree that it would be very helpful to include a figure with the partitioning of Fe-bound P and Fe from the model and have done so in reply to comment #12.

Comment #15:

The authors point out maxima in FeOx concentration at 21 cm and 60 cm in core NB8 (Fig. 5). On p. 13 lines 4-7 they attribute those maxima to peaks in Fe input to the estuary happening in 1977 and 1997 following years of low river flow (Fig. 2). They describe the river flow in 1977 and 1997 as high but actually the flow those years seems close to average, while the preceding years seemed to have distinctly low flow (Fig. 2).

Reply: This has been changed. See reply to comment #2.

Comment #16:

In addition to the concentration maxima at 21 cm and 60 cm, there was a high plateau in the total Fe profile before 1997. This suggests that there may have also been a sustained period of high Fe input before 1997. Is there evidence for sustained high input of Fe before 1997? Alternatively, could the total Fe profile suggest that the sediments may have become less oxidized after 1997, while sediment deposited before then retained a higher portion of refractory FeOx?

Reply: We have no evidence for a sustained period of high input of Fe prior to 1997. Instead, increased diagenetic remobilization of Fe following the enhanced organic matter input likely contributes to the contrast in total Fe above and below 21 cm. Indeed, sediments deposited prior to 1997 will have

retained a higher portion of Fe oxides. We now mention in the discussion that enhanced input of Fe and organic matter enhances conversion of Fe oxides to FeS.

“This increased input of Fe oxides and organic matter leads to enhanced conversion of Fe oxides to Fe sulfides.”

Comment #17

Large temporal changes in fluxes to the sediment were inferred from the model and the concentration profiles: Are these realistic?

Reply: Yes, we believe these are realistic, given that stream fluxes of total Fe and Mn in northern Sweden are known to be highly variable and show even larger seasonal changes (Björkvald et al., 2008). We added this information in the text (P.3 line 17-18).

In this region, the spring flood (April, May) is the major annual hydrological event. The spring flood results in a brief period of enhanced water flow in streams and rivers (Hölemann et al., 2005; Björkvald et al., 2008) and export of Fe and terrestrial organic matter to the coastal zone (refs). During high flow, total and dissolved Fe and Mn in streams can increase by a factor of up to 10, with concentrations being highly variable between years (Björkvald et al., 2008).

Comment #18:

After running the model to a steady state over 200 years, temporal changes in rates in input of various substances “were implemented to fit key porewater and solid phase depth profiles” (p. 8, line 17). This was also described by Rooze et al. (2016), the source of the model used here. It would be good to add some text describing how the input rates were fitted to the depth profiles. Was it a statistical approach such as regression? If so, are there statistical descriptions of the goodness of fit? The method of fitting was not mentioned in Rooze et al. (2016).

Reply: No statistical approach was used. The model was fitted to the data by visual observation. This is an approach that is applied broadly; for example

- Berg et, al. 2003; Dynamic Modeling of Early Diagenesis and Nutrient Cycling . a Case Study in an Arctic Marine Sediment; American Journal of Science
- Reed et, al. 2011; Sedimentary phosphorus dynamics and the evolution of bottom-water hypoxia: A coupled benthic-pelagic model of a coastal system; Limnology and Oceanography
- Dale et, al. 2013; Modeling benthic–pelagic nutrient exchange processes and porewater distributions in a seasonally hypoxic sediment: evidence for massive phosphate release by *Beggiatoa*?
- Reed et, al. 2011; A quantitative reconstruction of organic matter and nutrient diagenesis in Mediterranean Sea sediments over the Holocene; *Geochimica et Cosmochimica Acta*

We now added this information on P.7 line 15-16:

“The model was parameterized using data for NB8, information from the literature and by visually fitting modeled porewater and solid phase depth profiles to the measured data (model constrained; Table S.3).

Comment #19:

The relative magnitudes of the fitted changes in input rates (Fig. 3 and S.4) were generally larger than the fluctuations in river flows (Figs. 2 and S.8), which are suggested to partly account for the changes in input rates. Sedimentation rate was inferred to drop to a low rate from 2002-2015 (Fig. 3), during a period of relatively high flow for the Ore River (Fig. 2) as well as high flow for other Swedish Rivers (Fig. S.8). It seems more likely that sedimentation rate would increase during high river flow.

Reply: See reply to comment #2. Chemical processes on land are suggested to be the main driver of these changes (described on P2. Line 22-31). As a consequence, changes in input rates of elements can be larger than fluctuations in the river flow and may be partly decoupled from rates of sedimentation. The period of 2002-2015 is not characterized by an exceptionally high river flow. After the dry year in 1996, the flow returned to an average river flow, therefore no large changes in sedimentary input are expected.

Comment #20:

In some cases the inferred temporal patterns of inputs for different substances differ inexplicably. For example, input of FeOx peaks sharply from around 1997 when the sedimentation rate drops to a lower level (Fig. 3). Organic matter input follows a similar pattern. Does this imply that FeOx input is coupled with organic matter input but not with sedimentation rate?

Reply: See reply to comment #19. Indeed, Fe oxides and organic matter are strongly interlinked, as described in P.2 line 27-31. In this oligotrophic estuary, where the Ore River is the main source of both Fe and organic matter (P12 line 31-32), a similar pattern between input of Fe oxides and organic matter is expected. Because chemical processes on land are thought to be responsible for the variations in both the Fe and organic matter flux, this is not necessarily coupled to the input of other sedimentary material.

Comment #21:

The fluctuation in FeOx input seems to drive the assumed change in Fe:P ratios suggesting a partial decoupling of FeOx input from P input. Total Mn input follows a similar pattern as sedimentation rate. Does this suggest that Mn input is more related to sedimentation, while FeOx input is more related to organic matter input?

Reply: Processes on land can affect river fluxes of Fe to the coastal zone as described on P2. Line 22-31. However, this mechanism is probably different for manganese (Mn). While reduced species of Fe are expected to be oxidized during a dry period, in the case of Mn less reduced species are expected to be formed resulting in limited re-oxidation of Mn during a dry period. We now have added a sentence to explain this difference in riverine Fe and Mn input after a dry period:

P. 13 Lines 12-14:

“In contrast to Fe, limited re-oxidation of Mn is expected during a dry period because of less formation of reduced Mn species (Burdige 1993). Therefore, no strong increase in riverine Mn input is expected after a dry period.”

The coupling between Fe oxides and organic matter is described in the reply to comment #20.

Comment #22

Inputs of forms of organic matter with different reactivities show opposing temporal changes according to the model fit, with input of refractory organic matter dropping sharply just before 1990 while input of “less reactive” organic matter sharply increases. It may be possible that input of different forms of organic matter with differing reactivities could follow different temporal patterns. However, is it also possible that modeled reaction rates change in an unrealistic way at a certain depth in the sediment?

Reply: The degradation kinetics of the three types of organic matter are restricted by the need to be able to fit porewater profiles of ammonium, dissolved inorganic carbon and methane, which are all

determined by the degradation of organic matter. Further constraints are provided by the reaction kinetics and parameters from the literature (as described in Table S.7). This greatly limits the degrees of freedom while fitting. This is explained in detail by Van Cappellen and Wang (1996). We now added a sentence to the appendix (P. 1 line 35).

The large number of reactive species, which are coupled via modeled reactions and transport, greatly limits the variations in fitting reaction parameters (van Capellen and Wang 1996).

Comment #23:

Adjusting the rates of input of substances to the sediment to fit the concentration profiles is an interesting way to draw inferences about the temporal changes in the input rates. However, it seems possible that errors in modeling reactions at certain depths might lead to erroneous conclusions about temporal variations in inputs to the sediment. The authors should add some discussion of this.

Reply: See reply to comment #22 and reference to the work of Van Cappellen and Wang (1996) in the appendix (P.1 line 35). The kinetics of most chemical reactions used in the model are constrained by the literature (Table S.7). Further constraints are provided by the large number of model components and reactions that are modelled simultaneously and that are known to occur in these types of sediments. This makes the results quite robust. The approach we are using here is not unusual and has been applied in other studies to infer temporal changes in boundary conditions at the sediment-water interface (e.g. Berg et al., 2003; Reed et al., 2011; GCA, Dale et al., 2013). We find it difficult to identify and include consequences of “possible errors in modeling reactions” since there are no obvious candidates for such reactions.

Comment #24:

The temporal patterns for inputs of iron and organic matter based on the model in this paper are similar to those in Rooze et al. (2016). However, the model in this paper is adapted from Rooze et al. (2016) so the similarity of the predicted temporal patterns could reflect similar inaccuracies in the model at certain depths in the sediment that could erroneously suggest similar temporal variations in inputs to the sediment.

Reply: The specific model-code used in this study was adapted from Rooze et al. (2016). However, this is a standard reactive transport model using sets of reactions and transport equations that were first combined in such multi-component models more than two decades ago (e.g. Wang and Van Cappellen 1996 and additional references in the appendix) and have since then been used in a multitude of similar models. Reaction kinetics are based on extensive literature (Table S.7). This means that our results are not specific to this model code. We now have added a sentence in the model description section to explain this (p7, line 6): “This is a standard multi-component reactive transport model based on principles outlined by, for example, Wang and Van Cappellen (1996).”

Comment #25:

Instead of adjusting the rates of input of substances to the sediment to fit the concentration profiles the model could assume that the rates of inputs of all substances to the sediment are proportional to the sedimentation rate. I think that the text on p. 9, lines 15-17, indicates that this was done for the sensitivity analysis shown in Fig. 9. If so, it would mean that conclusions based on the analysis in Fig. 9 do not depend on the validity of the temporal variations in inputs that were fitted to the profiles. I suggest that the authors clarify this.

Reply: During the sensitivity analyses described on P.9 lines 15-17 input of Fe oxides, Mn oxides and organic matter were changed with the same factor as the sedimentation rate. However, the temporal variations as presented in Fig. 3 were still applied. A doubling of the sedimentation rate would then result in a doubling of the changes presented in figure 3. For clarity we changed the text on p. 9, lines 15-17: “Subsequently, a run was performed in which the temporal input of organic matter and Fe oxides (Fig. 3) both were changed by the same factor as the sedimentation rate to account for the role of rivers as the main source of material in the region (Algesten et al. 2006, Bjorkvald et al. 2008).”.

Comment #26:

The effect of salinity:

Section 5.4, p. 13 lines 25-27: This study highlights the role of bottom water salinity. “Because many studies focus on the relatively high salinity parts of estuaries... the role of vivianite as a sink for P has been largely overlooked.” This is true. However, Hartzell et al. (2017, cited on p.2 line 35) report SEDEX P fractions along estuarine salinity gradients from 0-11 with sedimentation rates ranging from 0.4-1.8 cm yr⁻¹. Their results were consistent with the model predictions in this paper. Although they did not identify vivianite in their sediments, they proposed that vivianite played an important role in P burial at low salinities in sediments rich in Fe²⁺.

Reply: We agree. Vivianite formation is indeed enhanced in environments where sulfide formation is relatively low compared to the input of Fe to the sediment. This is why we specifically included the Hartzell et al. reference in the introduction as key context for this work. We have now also included a reference to the Hartzell paper in the discussion (p12, line 17): “as vivianite (Rozan et al., 2002; Gächter and Müller, 2003; Hartzell et al., 2017). “

Detailed comments:

Comment #27

Abstract, lines 8 and 9: Add data on the measured salinity (5) and sedimentation rates (0.25-1.0 cm yr⁻¹) in parentheses.

Reply: The results which are described here are not based on measurements but on the modelled data, which cover a wider range than the measured in-situ data. For clarity, we prefer to not include these numbers here.

Comment #28

p. 5 line 6. Clarify what was analyzed by ICP-OES: “...dissolved... ..overnight. [The resulting solution was analyzed for] total element concentrations of...”

Reply: Sentence changed to: “Total elemental concentrations in the HNO₃ solution of Al, Fe, Mn, P and S were determined by ICP-OES.”

Comment #29:

p. 9 line 24: “Dissolved Fe²⁺ and Mn²⁺ profiles generally showed a maximum near the sediment-water interface.” This is in error. Actually, their concentrations were at a minimum near the surface, presumably due to oxidation.

Reply: The first point is the bottom water sample, hence our statement here is correct.

Comment #30:

p. 13, line 2: Should cite Fig. 5. Also, maxima at 42 cm are not distinct contrary to the statement in the text.

Reply: We now refer to figure 5 on P. 13, line 2. We removed “distinct” from this sentence.

Comment #31:

Fig. S. 5. Profiles of solids: Clarify the caption. Explain what FeOx 1 and FeOx 2 are. Also, note that the caption incorrectly states that the sum of these is graphed.

Reply: Text changed to: “Solid phase depth profiles of the easily reducible Fe oxides (Feox1) and reducible (crystalline) Fe oxides (Feox2) (and some vivianite), Fe carbonates (Fecarb), magnetite (Femag), elemental S (S0) and S in pyrite (CRS) for site NB8 in April 2015.”

Comment #32:

Consider moving Figs S.5 and S.7 to main text: They seem to present important information (S.5) and important model results (S.7). Fig S.5 seems to belong with Fig. 6. C7 Fig. S.7. seems to belong with Fig. 10 (which actually cites Fig. S.7. in the caption).

Reply: Figure S.5 contains the less important extraction data. For the readability of the paper we would prefer to keep this figure in the appendix. We now combined figure S.7 and Fig. 10 to make a new Fig. 10.

Jilbert, T., Asmala, E., Schröder, C., Tiihonen, R., Myllykangas, J. P., Virtasalo, J. J., ... & Hietanen, S. (2018). Impacts of flocculation on the distribution and diagenesis of iron in boreal estuarine sediments. *Biogeosciences*, 15, 1243-1271.

Response to Reviewer #2

Review of Lenstra et al. 2018 - Variations in river input of iron impact sedimentary phosphorus burial in an oligotrophic Baltic Sea estuary Decision I would be happy for this manuscript to be published after some minor corrections.

Manuscript Quality

The paper contributes knowledge of phosphorus burial a research largely overlooked in favour of carbon and nitrogen. The research focus on the main drivers of P burial in the northern Baltic sea, though a regional study this work will be of interest to a wide audience and highly relevant to Biogeosciences. The authors report that in this area a significant portion of the P burial is associated with vivianite crystallisation this coupled with they're model outputs highlight an important mechanism for P. Burial where increase in fresh riverine water and iron increase P burial.

The hydrological context of this research does need better clarification.

Visual Quality

Both the figures and tables are of high quality and are ready for publication.

Technical Quality

The methodologies they authors used were appropriate and applied correctly, I cannot comment on modelling. I would have liked to see the core chronologies in the main text not the Sup Mat but Table.1 does provide enough information.

Reply: We thank the anonymous referee for the positive remarks. We reply to the comments below and have revised the manuscript accordingly. Where the comments of reviewer #2 overlap with those of reviewer #1, we have indicated this.

Comment #1:

Major Comments

Clarify if the flow measurement were made for the Ore river as the title and abstract suggest that the authors are directly linking river input and P burial but this is not supported by the data.

Reply: See reply to comment #1 of reviewer #1. We agree with the reviewer that measurements of riverine Fe input would form a useful addition. Unfortunately, long term measurements of total Fe input are not available for the Ore River (or any other rivers in the region) and therefore cannot be included in our manuscript. However, by modelling key porewater and solid phase depth profiles in the Ore Estuary, we demonstrate that large temporal changes in Fe and organic matter input are necessary to fit our model to the measured data at this site (section 3.4). Because this is such an oligotrophic coastal region, the large temporal changes in Fe and organic matter input to sediments located at a river mouth can only be explained by variations in river input.

We therefore would strongly prefer to keep our title as it is but refer this point to the editor. If the editor would like us to change the title we will change it to: "Variations in iron input impact sedimentary phosphorus burial in an oligotrophic Baltic Sea estuary".

Comment #2:

The data from the Ore river does differ from the averaged flows from the 86 other river is there a reason for this. Is the Ore and its catchment an oddity or is it comparable to other estuaries in the area.

Reply: See reply to comment #3 of reviewer #1. Spatial and temporal patterns of rainfall over Sweden are expected to differ and result in differences in river discharge between the 86 rivers and the Ore River. Meltwater, for example, plays a more important role for rivers at high latitudes when compared to lower latitudes. As described on P.13 in lines 4-11, the 1996 dry period affected the whole Baltic Sea. This was less so for 1976.

Comment #3:

The authors have cores from 5 sites (NB1,6,7,8 and 10) but only model site NB8. Is there a reason for this and how comparable are the different sites. From Fig.5 it is clear that all the data falls within the same ranges but NB8 is the furthest from the river mouth and a clear statement on why the model was applied to only this site would be useful.

Reply: See reply to comment #7 of reviewer #1. In this study we wished to assess the burial of P in and below the SMTZ and the factors contributing to temporal variations in P burial, including the role of the rate of sedimentation. As we were not able to sample below the SMTZ at sites NB1, N6 and N10 (April)

and the geochemistry of sites N7 and NB8 is comparable, we focused on site NB8. At site NB8 we subsequently performed three types of chemical extractions and experimental work to allow for visual observations of vivianite. We did not obtain these data for the other sites. The geochemistry at site NB8 is strikingly similar to that at another site with a high sedimentation rate in the Bothnian Sea (Egger et al., 2015a, b), as is discussed in the manuscript (e.g. p2, lines 15-17).

We have changed the text in the model description section to clarify that we selected NB8 because it has a shallow SMTZ and a relatively high sedimentation rate (P.7 line 3-4): “Site NB8 was characterized by a SMTZ close to the sediment-water interface and a relatively high sedimentation rate (Table 1).”

Comment #4:

One important question that seems to have not been mentioned is the potential for the Fe-P to be bound to FeOx. I think an additional figure illustrating downcore profile of Total Fe, FeOC, Fe-P and possibly vivianite bound P and organics.

Reply: In the extraction methods that we used there is not a specific step, which only extracts vivianite. In the SEDEX vivianite is extracted together with P bound to Fe oxides (Dijkstra et al., 2014, Nembrini et al., 1983). In the Fe extraction vivianite is extracted in both the HCl-Acetate and CDB step (Dijkstra et al. 2014). Therefore a single figure containing measured data of P bound to vivianite and P bound to Fe oxides is not possible. However, with the model we can make the distinction between these phases. Therefore we added a figure to the appendix (Fig. S.7), which shows the change in Fe bound in vivianite and Fe oxides as well as P bound to vivianite and Fe oxides. We now describe the figure in the results (p10, line 29): “At depth, P bound to vivianite becomes more important compared to P bound to Fe oxides (Fig. S.7).”

The relative contribution of Fe-oxide bound P and vivianite is discussed in lines 9-11 on page 12. “Due to dissolution of Fe oxides and vivianite formation in the sediment the fraction of P bound to vivianite increases with depth (Fig. S.7).”

Comment #5:

Again line 4 Pg 13 – the refer to the years of 1977 and 1997 as high flow years but both looking at the Ore flow rates and S.Fig8 I would say that they have larger flows. I would focus more of the low flow years proceeding as the major mechanism.

Reply: See reply to comment #2 of reviewer #1. We agree that the river flow in the years after each relatively dry period (1976 and 1996) was not exceptionally high. The mechanisms that we propose in this manuscript as a reason for the enhanced input of Fe depend on the relatively low river flow in the years 1976 and 1996 being followed by a higher flow when directly compared to the preceding dry period. For clarity we changed the text:

P2. Line 25 from “In ensuing wet periods” to “After dry periods”

P.13 S.5 from “In the following wet years,” to “in the following years”.

P14 S.14 from “in a wet period directly following a dry period on land in 1976 and 1996,” to “in a period following a dry year on land in 1976 and 1996”.

Comment #6:

Along the same lines do you have any rainfall data for this period this could be useful in further contextualising the low flows. A quick look at the UEA North Atlantic Oscillation records <https://crudata.uea.ac.uk/cru/data/nao/nao.dat> both 1976 and 1996 were in the negative phase

meaning dry conditions for the higher latitudes. In particular 1996 was in a very strong negative phase (NAO index:-3.27) explaining the low flows. Work completed in Scottish fjords (restricted marine environments not too dissimilar to the research area) showed that during negative NAO phases material builds up in the catchment and when the NAO switches that store of material is quickly transported to the sea – This mechanism may explain the increases in FeOx after the dry/low flow periods.

Gillibrand, PA, Cage, AG & Austin, WEN 2005, 'A preliminary investigation of basin water response to climate forcing in a Scottish fjord: evaluating the influence of the NAO' Continental Shelf Research, vol. 25, pp. 571-587. DOI: 10.1016/j.csr.2004.10.011

Reply: We agree with the reviewer that the NOA could play an important role in regulating the amount of precipitation on land, the related changes in Fe chemistry and the subsequent transfer of Fe to estuaries. We have now added a reference to the work of Gillibrand et al. (2005) and state that periods of low rainfall may be related to a negative phase in the North Atlantic Oscillation. We could not find any mention of particulate matter in the cited study.

Revised text (P13. Line 5): "We suggest that these high inputs of Fe and organic matter are directly linked to variations in river discharge, that may be linked to negative phases in the North Atlantic Oscillation (Gillibrand et al. 2005)".

Comment #7:

The authors do focus on the role of salinity as a key component of the P burial process but as the modelling only takes place at the most saline site is the importance of this overestimated. Clarification would be useful.

Reply: The salinity at all sites was comparable (~5), therefore an overestimation is not expected. It would be interesting to also sample sites with fine-grained sediments and a lower bottom water salinity. These types of sites were, however, not found in the Ore Estuary. To obtain insight in the role of salinity, we performed a sensitivity analysis (Fig. 9). Our results highlight that a lower salinity would increase the role of vivianite formation.

Changes made:

Change the title to: "Variations in iron input impact sedimentary phosphorus burial in an oligotrophic Baltic Sea estuary".

P2. Line 25 changed from "In ensuing wet periods" to "After dry periods"

P.13 S.5 changed from "In the following wet years," to "in the following years".

P14 S.14 changed from "in a wet period directly following a dry period on land in 1976 and 1996," to "in a period following a dry year on land in 1976 and 1996"

We now mention this in section 2.1 (Lines 18-19): "While surface water salinity varies with time and distance from the river, there is no salinity gradient in the bottom water of this estuary. The spatial extent of the particle plume from the river varies with time but is known to reach all of our sample sites (Malmgren & Brydsten, 1992). "

We have modified the text (P1. lines 10-11) to clarify that input of Fe and organic matter is enhanced after dry periods: "Distinct enrichments in sediment Fe and sulfur at depth in the sediment are attributed to short periods of enhanced input of riverine Fe and organic matter. These periods of enhanced input are linked to variations in rainfall on land and follow dry periods."

We have changed the text in the model description section to clarify that we selected NB8 because it has a shallow SMTZ and a relatively high sedimentation rate (P.7 line 3-4): "Site NB8 was characterized by a SMTZ close to the sediment-water interface and a relatively high sedimentation rate (Table 1)."

p. 7 line 15: We now explicitly mention site NB8 in this sentence: "The model was parameterized using data site NB8,"

We have now added text on page 8 to explain this (line 27): "This assumption is based on the dominance of natural forest and wetlands in the region (Björkvald et al., 2008). We note that the model results were very sensitive to the P:Fe ratio and that we could not model the key profiles when assuming a higher P:Fe ratio".

We have now changed Figure 6 and its caption and our method section to convey that vivianite Fe is also extracted in the HCl and CDB steps (p5, lines 11-13).

We have now also added a figure showing this relative distribution, both for Fe and P, as calculated with the model (Fig. S.7) and corresponding text in the results (p10, line 29): "At depth, P bound to vivianite becomes more important compared to P bound to Fe oxides (Fig. S.7)."

The relative contribution of Fe-oxide bound P and vivianite is discussed in lines 9-11 on page 12. "Due to dissolution of Fe oxides and vivianite formation in the sediment the fraction of P bound to vivianite increases with depth (Fig. S.7)."

We now mention in the discussion that enhanced input of Fe and organic matter enhances conversion of Fe oxides to FeS. P.13 lines 7-10

"This increased input of Fe oxides and organic matter leads to enhanced conversion of Fe oxides to Fe sulfides."

We added this information in the text (P.3 line 17-18).

In this region, the spring flood (April, May) is the major annual hydrological event. The spring flood results in a brief period of enhanced water flow in streams and rivers (Hölemann et al., 2005; Björkvald et al., 2008) and export of Fe and terrestrial organic matter to the coastal zone (refs). During high flow, total and dissolved Fe and Mn in streams can increase by a factor of up to 10, with concentrations being highly variable between years (Björkvald et al., 2008).

We now added information on P.7 line 15-16:

“The model was parameterized using data for NB8, information from the literature and by visually fitting modeled porewater and solid phase depth profiles to the measured data (model constrained; Table S.3).

P. 13 Lines 12-14:

“In contrast to Fe, limited re-oxidation of Mn is expected during a dry period because of less formation of reduced Mn species (Burdige 1993). Therefore, no strong increase in riverine Mn input is expected after a dry period.”

We now added a sentence to the appendix (P. 1 line 35).

The large number of reactive species, which are coupled via modeled reactions and transport, greatly limits the variations in fitting reaction parameters (van Capellen and Wang 1996).

We now have added a sentence in the model description section to explain this (p7, line 6): “This is a standard multi-component reactive transport model based on principles outlined by, for example, Wang and Van Cappellen (1996).”

For clarity we changed the text on p. 9, lines 15-17: “Subsequently, a run was performed in which the temporal input of organic matter and Fe oxides (Fig. 3) both were changed by the same factor as the sedimentation rate to account for the role of rivers as the main source of material in the region (Algesten et al. 2006, Bjorkvald et al. 2008).”.

(p12, line 17): “as vivianite (Rozan et al., 2002; Gächter and Müller, 2003; Hartzell et al., 2017). “

P.6 line 6: Sentence changed to: “Total elemental concentrations in the HNO₃ solution of Al, Fe, Mn, P and S were determined by ICP-OES.”

We now refer to figure 5 on P. 13, line 2. We removed “distinct” from this sentence.

Caption of figure S.5: “Solid phase depth profiles of the easily reducible Fe oxides (Feox1) and reducible (crystalline) Fe oxides (Feox2) (and some vivianite), Fe carbonates (Fecarb), magnetite (Femag), elemental S (S0) and S in pyrite (CRS) for site NB8 in April 2015.”

Figure S.5 contains the less important extraction data. For the readability of the paper we would prefer to keep this figure in the appendix. We now combined figure S.7 and Fig. 10 to make a new Fig. 10.

Revised text (P13. Line 5): “We suggest that these high inputs of Fe and organic matter are directly linked to variations in river discharge, that may be linked to negative phases in the North Atlantic Oscillation (Gillibrand et al. 2005)”.

Large variations in iron input to an oligotrophic Baltic Sea estuary: impact on sedimentary phosphorus burial

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Abstract. Estuarine sediments are key sites for removal of phosphorus (P) from rivers and the open sea. Vivianite, an iron (Fe)(II)-P mineral, can act as a major sink for P in Fe-rich coastal sediments. In this study, we investigate the burial of P in the Öre Estuary in the northern Baltic Sea. We find much higher rates of P burial at our five study sites (up to $\sim 0.145 \text{ mol m}^{-2} \text{ yr}^{-1}$) when compared to more southern coastal areas in the Baltic Sea with similar rates of sedimentation. Detailed study of the sediment P forms at our site with the highest rate of sedimentation reveals a major role for P associated with Fe and the presence of vivianite crystals below the sulfate methane transition zone. By applying a reactive transport model to sediment and porewater profiles for this site, we show that vivianite may account for up to $\sim 40\%$ of total P burial. With the model, we demonstrate that vivianite formation is promoted in sediments with a low bottom water salinity and high rates of sedimentation and Fe oxide input. While high rates of organic matter input are also required, there is an optimum rate above which vivianite formation declines. Distinct enrichments in sediment Fe and sulfur at depth in the sediment are attributed to short periods of enhanced input of riverine Fe and organic matter. These periods of enhanced input are linked to variations in rainfall on land and follow dry periods. Most of the P associated with the Fe in the sediment is likely imported from the adjacent eutrophic Baltic Proper. Our work demonstrates that variations in land-to-sea transfer of Fe may act as a key control on burial of P in coastal sediments. Ongoing climate change is expected to lead to a decrease in bottom water salinity and contribute to continued high inputs of Fe oxides from land, further promoting P burial as vivianite in the coastal zone of the northern Baltic Sea. This may enhance the role of this oligotrophic area as a sink for P imported from eutrophic parts of the Baltic Sea.

1 Introduction

Phosphorus (P) is an important nutrient for primary producers. Burial of reactive P (i.e. bioavailable P) in coastal sediments can permanently remove P from the water column (Froelich et al., 1982; Delaney, 1998; Ruttenger, 2003). This removal allows coastal systems to act as a filters for P, reducing the flux of land-derived P to the open sea (Froelich, 1988; Bouwman et al., 2013; Asmala et al., 2017), and as sinks of P imported from the open sea (Asmala et al., 2017). The major sedimentary phases

contributing to the removal of reactive P in coastal sediments are organic-P, iron-bound P and authigenic calcium (Ca)-bound P (Ruttenberg and Berner, 1993; Slomp et al., 1996a).

In most coastal systems, organic matter is a major carrier of P to the sediment (Slomp, 2011). The subsequent microbial degradation of part of the organic matter can lead to elevated concentrations of phosphate (HPO_4^{2-}) in the porewater and precipitation of authigenic P minerals (Froelich et al., 1988; Ruttenberg, 2003). While until recently carbonate fluorapatite was thought to act as the major sink of P in coastal systems (Ruttenberg and Berner, 1993; Slomp et al., 1996b; Ruttenberg, 2003), increasing evidence points towards a significant role for the Fe(II)-phosphate mineral vivianite (Slomp et al., 2013; Egger et al., 2015a; Li et al., 2015; Dijkstra et al., 2016).

Vivianite can form in sediments where the supply of sulfate (SO_4^{2-}) is low relative to the input of Fe(oxyhydr)oxides (henceforth termed Fe oxides). As a consequence, not all Fe oxides are converted to Fe sulfides (FeS and FeS_2) (Ruttenberg, 2003) and Fe oxides can continue to dissolve at depth through Fe reduction coupled to organic matter degradation or anaerobic oxidation of methane ("iron-AOM"; Beal et al. (2009); Egger et al. (2015b); Ettwig et al. (2016)). In coastal sediments, conditions for the formation of vivianite are especially favorable below the sulfate methane transition zone (SMTZ) (Roden and Edmonds, 1997; März et al., 2008; Hsu et al., 2014; Egger et al., 2015a). Here, both porewater Fe^{2+} and HPO_4^{2-} can accumulate in the absence of sulfide and precipitate as vivianite (Ruttenberg, 2003; Egger et al., 2015a; Dijkstra et al., 2016). Therefore, sediments with high rates of sedimentation and inputs of organic matter and Fe oxides and with an SMTZ that is close to the sediment-water interface are thought to be particularly conducive to vivianite formation (Slomp et al., 2013; Egger et al., 2015a).

Recent studies of diagenesis in sediments of the northern Baltic Sea indicate that variations in the input of organic matter and Fe oxides may contribute to temporal variations in vivianite formation in coastal sediments (Egger et al., 2015a; Rooze et al., 2016). While Egger et al. (2015a) attributed this to eutrophication, the large magnitude of the change in input of organic matter and of Fe required to describe these data with a reactive transport model (a factor of 15 and 2, respectively; Rooze et al. (2016)) suggests that additional processes are active. We hypothesize that variations in river input of both organic matter and Fe, linked to variations in river discharge, play a role. This hypothesis is based on observed changes in Fe dynamics in soils and rivers in Finland (Sarkkola et al., 2013). More specifically, dry periods may lower groundwater levels exposing Fe minerals in previously reducing soil layers to oxidation (Laudon et al., 2011). After dry periods, the freshly formed Fe oxides can be reduced again, after which Fe can be mobilized as Fe^{2+} and transported to rivers and the coastal zone (Sarkkola et al., 2013). While some of the Fe^{2+} will be oxidized to form amorphous and crystalline Fe oxides (Schwertmann and Taylor, 1989; Pokrovsky and Schott, 2002) and will be transported downstream in particulate form, some of the Fe^{2+} can also form complexes with dissolved organic compounds and remain in solution (Rue and Bruland, 1995; Wu and Luther, 1995; Kuma et al., 1996). Both the particulate and dissolved Fe and the associated organic matter may be transported to the coastal zone through river flow where they may impact P burial.

Future climate change is expected to alter precipitation patterns in Northern Europe and change both the magnitude and seasonality of river discharge (Harley et al., 2006). In the northern Baltic Sea, an increase in the input of freshwater is expected over the coming century (Meier et al., 2006). Such a change may further promote vivianite formation by reducing the availability of SO_4^{2-} (Jordan et al., 2008; Hartzell et al., 2017). Environmental change may also alter riverine input of Fe. In

the northern Baltic Sea, the input of dissolved Fe from rivers has increased over the past decades (Kritzberg and Ekström, 2012; Sarkkola et al., 2013; Björnerås et al., 2017). The associated increased input of Fe oxides to coastal sediments may also enhance vivianite formation.

In this study, we investigate the burial of P in the Öre Estuary in the northern Baltic Sea, with a specific focus on the factors contributing to vivianite formation. Porewater and sediment geochemical depth profiles for five sites characterized by varying rates of sedimentation are presented. We apply a reactive transport model to the data for one of the sites and investigate how vivianite formation and P burial in the sediment responds to changes in (1) bottom water salinity, (2) sedimentation rate (3) the input of Fe oxides and (4) the input of organic matter. We also discuss the expected changes in the burial of P in coastal sediments upon ongoing climate change. Our model results suggest that vivianite will become a more important sink for P in the coastal zone of the Baltic Sea in future because of the expected decline in salinity and the continued high input of Fe from land.

2 Methods

2.1 Study area and sampling

The Öre Estuary is located along the Swedish coast in the Bothnian Sea, in the northern Baltic Sea (Fig. 1). The estuary is oligotrophic and has a surface area of approximately 70 km², a mean depth of 10 m and a bottom water salinity of ca. 5 (www.SMHI.se). The estuary is fed by the Öre River, which has a strongly varying rate of annual discharge (Fig. 2). While surface water salinity varies with time and distance from the river, there is no salinity gradient in the bottom water of this estuary. The spatial extent of the particle plume from the river varies with time but is known to reach all of our sample sites (Malmgren and Brydsten, 1992). In this region, the spring flood (April, May) is the major annual hydrological event. The spring flood results in a brief period of enhanced water flow in streams and rivers (Hölemann et al., 2005; Björkvald et al., 2008) and export of Fe and terrestrial organic matter to the coastal zone (Rember and Trefry, 2004; Algesten et al., 2006). During high flow, total and dissolved Fe and Mn in streams can increase by a factor of up to 10, with concentrations being highly variable between years (Björkvald et al., 2008).

This study focuses on sediments from five sites in the Öre Estuary (Fig. 1B), with water depths varying from 10 to 33 m (Table 1). Sediments at all sites are fine-grained and rich in organic matter (Hellemann et al. (2017); Table 1). The major macrofauna species in the area are the mollusk *Limecola balthica* (formerly named *Macoma balthica*), the amphipod *Monoporeia affinis*, the spionid *Marenzelleria* spp. and the isopod *Saduria entomon* (Fig. S.1). *Marenzelleria* first appeared in 1995, but only became abundant after 2002/2003, with densities at our study sites ranging from 187 to 780 ind m⁻² (Kauppi et al., 2015). The density of *Marenzelleria* spp. in the sediment is water depth dependent with maximum densities at water depths between 30 and 50 meters and lower densities both above and below (Kauppi et al., 2015).

Sediment was collected during two field campaigns with *R/V Lotty* in April and August 2015 using a Gemini gravity corer (8 cm inner diameter). In April, three cores were taken per site. The first core was used for porewater and solid phase analyses, the second core was used for methane (CH₄) sampling and the third core for sediment dating using ²¹⁰Pb. In August, two cores

were collected per site for porewater analyses and for CH₄. At site NB8, a third and a fourth core were collected in August for mineral analyses and additional ²¹⁰Pb measurements.

Methane was sampled directly after core recovery using a core liner with pre-drilled holes with a 2.5 cm depth-spacing. Samples of 10 ml were taken with cutoff syringes from each hole and immediately transferred to a 65 ml glass bottle filled with saturated salt solution. The bottles were stoppered, capped and stored upside down until analysis.

After core retrieval, two bottom water samples were taken and subsequently the cores were sliced into intervals of 1 to 4 cm under a nitrogen atmosphere at bottom water temperature (Table 1). Each sediment sample was divided over a pre-weighed glass vial for solid phase analysis and determination of water content, and a 50 ml centrifuge tube. The glass vials were stored in nitrogen flushed gas-tight aluminum bags at -20°C until analysis. The 50 ml centrifuge tubes were centrifuged at 3500 rpm for 20 minutes to extract porewater.

2.2 Bottom water and porewater analyses

Bottom and porewater samples were filtered through 0.45 µm pore size filters and subsampled under a nitrogen atmosphere. Subsamples were taken for analysis of SO₄²⁻, hydrogen sulfide (where H₂S represents the sum of H₂S, HS⁻ and S²⁻), Fe, manganese (Mn), HPO₄²⁻, ammonium (NH₄⁺) and dissolved inorganic carbon (DIC). Total Fe and Mn are assumed to represent Fe²⁺ and Mn²⁺, although in the latter case some Mn³⁺ may also be included (Madison et al., 2011). Subsamples for NH₄⁺ were stored frozen at -20°C. All other subsamples were stored at 4°C until analysis. Samples for SO₄²⁻ were analyzed with ion chromatography (detection limit of <75 µmol L⁻¹; average analytical uncertainty based on duplicates and triplicates <2%). For H₂S, 0.5 ml of porewater was immediately transferred into a 4 ml glass vial containing 2 ml of 2% zinc acetate solution to trap the H₂S as ZnS. Sulfide was determined spectrophotometrically by complexation of the ZnS precipitate in an acidified solution of phenylenediamine and ferric chloride (Cline, 1969). The sulfide standard was verified by titration with thiosulfate. Subsamples taken for porewater Fe²⁺, Mn²⁺ and HPO₄²⁻ were acidified with 10 µL 30% suprapur HCl per ml of sample and were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES; Spectro Arcos).

Concentrations of NH₄⁺ were determined with the modified indophenol-blue method (Solorzano, 1969). Samples for DIC analyses were collected in 5 mL vials without a headspace and poisoned with 10 µL of saturated HgCl₂. Analysis for DIC was performed using an AS-C3 analyzer (Apollo SciTech), consisting of an acidification and purging unit in combination with a LICOR-7000 CO₂/H₂O Gas Analyzer.

Samples for CH₄ were prepared for measurement by injecting a 10 ml nitrogen headspace into the bottle. Subsequently, the CH₄ concentrations in the headspace were determined by injection of a subsample (50-200 µL) into a Thermo Finnigan Trace GC gas chromatograph (Flame Ionization Detector), after which calculated CH₄ concentrations were corrected for sediment porosity. The average analytical uncertainty based on duplicates and triplicates was <3% for DIC and <5% for CH₄.

2.3 Solid phase analyses

Sediments were freeze-dried and the porosity was determined from the weight loss upon freeze drying. Freeze-dried sediments were ground in an agate mortar under a nitrogen atmosphere and were split into subsamples, that were stored either under oxic

or anoxic conditions. For site NB8, the speciation of solid phase Fe, S and P was determined on the anoxic subsamples to avoid oxidation artifacts (Kraal et al., 2009; Kraal and Slomp, 2014). All other analyses were performed on the oxic subsamples.

Ca. 300 mg of sediment was decalcified with two wash steps of 1 M HCl (Van Santvoort et al., 2002) and subsequently dried, powdered and analyzed for carbon using an elemental analyser (Fison Instruments model NA 1500 NCS). Organic carbon (C_{org}) contents were determined after correction for the weight loss during decalcification. The average analytical uncertainty based on duplicates and triplicates was <5%. A second subsample of ca. 125 mg was digested in 2.5 ml of HClO₄ and HNO₃ (ratio 3:2) and 2.5 ml 40% HF in a teflon vessel at 90°C overnight. The acid was evaporated at 140°C until a gel was formed, which was subsequently dissolved in 25 ml of 4.5% HNO₃ at 90°C overnight. Total elemental concentrations in the HNO₃ solution of Al, Fe, Mn, P and S were determined by ICP-OES, from which total concentrations in the sediment samples were calculated. The average analytical uncertainty based on duplicates and triplicates was <3% for all reported elements.

Sediment samples of ca. 50 mg were subjected to the 4-step Fe speciation procedure of (Poulton and Canfield, 2005) that targets the following Fe phases: (i) carbonate associated Fe (including siderite and ankerite), extracted for 24 hours with 1 M Na-acetate (pH brought to 4.5 with acetic acid); (ii) easily reducible Fe oxides and vivianite (including ferrihydrite and lepidocrocite), extracted for 24 hours with 1 M hydroxylamine-HCl in 25% v/v acetic acid; (iii) reducible (crystalline) Fe oxides and vivianite (including goethite, hematite and akagenéite), extracted for two hours with Na-dithionite (pH 4.8); (iv) recalcitrant Fe oxides (mainly magnetite), extracted for two hours with 0.2 M ammonium oxalate/0.17 M oxalic acid. Samples were measured colorimetrically using the 1,10-phenanthroline method (APHA, 2005). For simplicity, fractions (ii) and (iii) were summed and henceforth referred to as total Fe oxides. Average analytical uncertainty, based on duplicates, was <5% for all fractions.

Sediment samples of ca. 500 mg were subjected to the 3-step S speciation procedure of (Burton et al., 2006, 2008) that targets the following S phases: (i) acid volatile sulfur (AVS, i.e. mostly FeS) by addition of 2 ml of ascorbic acid and 10 ml of 6 M HCl to the sediment and trapping of the released H₂S into a tube filled with 7 ml Zn-acetate; (ii) elemental sulfur (S⁰) by extracting overnight with 25 ml methanol; (iii) chromium reducible sulfur (CRS, i.e. mostly FeS₂) by addition of acidic chromium chloride solution and trapping of the released H₂S into a tube filled with 7 ml Zn-acetate. Samples for AVS and CRS were analyzed by iodometric titration of the alkaline Zn-acetate trap. Elemental sulfur was measured colorimetrically according to Bartlett and Skoog (1954). Average analytical uncertainty, based on duplicates, was <3% for all fractions.

Sediment samples of ca. 100 mg were subjected to the SEDEX method described by Ruttenger (1992) as modified by Slomp et al. (1996a), but including the exchangeable P step. Five P phases were distinguished: (i) exchangeable-P, extracted for 30 minutes with 1 M MgCl₂ (pH 8); (ii) Fe-bound P fraction (including Fe oxide bound P and vivianite; Nembrini et al. (1983); Dijkstra et al. (2014)) extracted for 8 hours with citrate-dithionite-bicarbonate (CDB) (pH 7.5) followed by extraction for 30 minutes with 1 M MgCl₂ (pH 8); (iii) authigenic Ca-P (including carbonate fluorapatite, biogenic hydroxyapatite and carbonate-bound P), extracted for 6 hours with Na-acetate buffer (pH 4) followed by extraction for 30 minutes with 1 M MgCl₂ (pH 8); (iv) detrital Ca-P, extracted for 24 hours with 1 M HCl; (v) organic P, extracted for 24 hours with 1 M HCl after ashing at 550°C for 2 hours. Steps (i)-(iv) were performed under an argon atmosphere to avoid oxidation artefacts (Kraal et al., 2009;

Kraal and Slomp, 2014). CDB solutions were analyzed for P with ICP-OES. All other solutions were measured colorimetrically according to Strickland and Parsons (1972). Average analytical uncertainty, based on duplicates, was <5% for all fractions.

2.4 Sedimentation rate and P burial

Sediment accumulation rates at all 5 sites were determined from depth profiles of ^{210}Pb for April (NB1, N6, N10 and N7) or August (NB8). ^{210}Pb was measured on freeze dried sediment by direct gamma counting at 46.5 keV using a high purity germanium detector (Ortec GEM-FX8530P4-RB). Self-absorption was measured directly and the detector efficiency was determined by counting a National Institute of Standards and Technology sediment standard. Excess ^{210}Pb was calculated as the difference between the measured total ^{210}Pb and the estimate of the supported ^{210}Pb activity as given by ^{214}Pb ($^{210}\text{Pb}_{\text{exc}} = ^{210}\text{Pb}_{\text{total}} - ^{214}\text{Pb}$). Sediment accumulation rates at each site were estimated by fitting a reactive transport model (Soetaert and Herman, 2008) to the ^{210}Pb depth profiles assuming depth dependent changes in porosity and bioturbation (Fig. S.2).

Total P burial ($\text{mol m}^{-2} \text{ yr}^{-1}$) for all sites was calculated as follows:

$$P_{\text{burial}} = P_{\text{total}} * \text{sed.rate} * \rho * (1 - \phi) * 10^4 \quad (1)$$

where P_{total} is the averaged concentration of total P (mol g^{-1}) over the deepest 10 cm of the sediment sampled, ϕ is the porosity in the same interval (vol vol^{-1}), sed. rate is the sedimentation rate (cm yr^{-1}) and ρ is the density of dry sediment, 2.65 g cm^{-3} (Burdige, 2006).

2.5 Scanning electron microscopy (SEM)

Sediment samples from site NB8 were analyzed by SEM to determine whether large vivianite crystals ($\geq 38 \mu\text{m}$ size) were present. Wet sediments from five depths (sediment depth intervals: 3–4 cm, 14–16 cm, 34–36 cm, 49–52 cm and 55–58 cm) were sieved through a $38 \mu\text{m}$ mesh size sieve under an argon atmosphere with deoxygenated ultraclean water. The sieved material was washed seven times (5 minutes) with deoxygenated ultraclean water in a sonic bath. After washing, the samples were dried in an argon filled glovebox at ambient temperature. A subsample of the sieved and dried material was mounted on an aluminum sample holder using double sided carbon tape and subsequently coated with 0.8 mm platinum. Samples were analyzed using SEM-energy dispersive X-ray spectroscopy (EDS; JCM 6000PLUS NeoScope Benchtop SEM) with 15 kV accelerating voltage using a Si/Li detector, in scanning electron mode. Measurements with EDS were performed in the 0–20 keV energy range for elemental quantification (probe current: 1 nA; acquisition time: 50 s (live time)). SEM-EDS software was used to estimate the relative abundances in mol% for the major elements (oxygen (O), sodium (Na), magnesium (Mg), Al, silica (Si), P, calcium (Ca), Mn, Fe). Samples were detected and photographed in secondary electron imaging (SEI) mode. Measurements were performed with a $1 \mu\text{m}$ beam in backscatter mode imaging (BEI).

3 Reactive transport modeling

3.1 General model description

To investigate the mechanisms that control the formation of vivianite in the Öre Estuary a reactive transport model was applied to key porewater and solid phase depth profiles for site NB8. Site NB8 was characterized by a SMTZ close to the sediment-water interface and a relatively high sedimentation rate (Table 1). The model describes the mass balance of 11 dissolved and 18 particulate species (Table S.1) and is a modified version of that of Rooze et al. (2016), extended here to include the sedimentary Mn cycle. This is a standard multi-component reactive transport model based on principles outlined by, for example, Wang and Van Cappellen (1996). Three forms of Mn are distinguished, namely Mn oxides, Mn carbonate and Mn^{2+} . The transformations of Mn that are included are Mn carbonate and Mn oxide formation and Mn oxide reduction coupled to either H_2S , Fe^{2+} or CH_4 oxidation (Table S.2; R25-R32).

The model domain consists of a one-dimensional grid of 900 evenly distributed cells that captures the interval from the sediment-water interface to a depth of 90 cm. All chemical species are subject to biogeochemical reactions (Table S.2). Solids and solutes are transported by sediment accumulation and bioturbation. Solutes are additionally transported by molecular diffusion and bioirrigation (Soetaert et al., 1996; Wang and Van Cappellen, 1996; Boudreau, 1997). Bioirrigation is modeled as a non-local exchange process (Boudreau, 1984; Emerson et al., 1984).

3.2 Model Parameterization

The model was parameterized using data for site NB8, information from the literature and by visually fitting modeled porewater and solid phase depth profiles to the measured data (model constrained; Table S.3). Environmental parameters such as porosity, temperature, salinity and bottom water solute concentrations were measured (Table S.4; Fig. S.3A). The density of dry sediment and the C:N ratio for organic matter were taken from literature (Redfield, 1958; Burdige, 2006). Bioturbation and bioirrigation coefficients were used as fitting parameters (Fig. S.3B&C), taking into account when the most important biorrigator in these sediments, *Marenzelleria* spp., established (Fig. S.1) and the typical range in these coefficients at similar macrofaunal densities (Renz and Forster, 2013). Fluxes of solids at the sediment-water interface were model constrained. A detailed description of the reactive transport model is given in the supplements.

3.3 Iron, manganese and phosphorus dynamics

In the model, Fe oxides and Mn oxides are assumed to consist of fractions with different crystallinities, which affect their reactivity towards organic matter and H_2S (Table S.1). In both cases, a highly reactive fraction (α) and a less reactive fraction (β) are assumed, whereas for Fe oxides also a refractory fraction (γ) is included. Only the α fraction of the Fe oxides and Mn oxides is susceptible to reductive dissolution linked to degradation of OM. This allows the β fraction to be buried below the zone of organic matter degradation (Rooze et al., 2016).

Reactive P is deposited at the sediment-water interface in the form of organic-P and Fe oxide bound P. For organic matter three fractions are assumed: a highly reactive (α), less reactive (β) and refractory (γ) fraction, following the multi-G approach (Jørgensen, 1978; Westrich and Berner, 1984; Middelburg, 1989). The C:P ratio is 300:1 for all three fractions of organic matter and is model constrained. This relatively high and constant value for the C:P ratio is based on the refractory nature of the organic matter in the area (Stockenberg and Johnstone, 1997; Algesten et al., 2006; Leipe et al., 2011). The three fractions of Fe oxides are assumed to have different P:Fe ratio's, with highly reactive Fe oxides having a higher P:Fe ratio than less reactive crystalline Fe oxides assuming the former can bind more P (Table S.3; Gunnars et al. (2002)). In the bioirrigated zone, porewater HPO_4^{2-} is assumed to bind to the Fe oxide $^\beta$ fraction present (Fig. S.3C&D) to a maximum P:Fe ratio of 0.28 (mol mol^{-1} ; Table S.3). This allows for enhanced formation of Fe oxide bound P due to bioirrigation (Norkko et al., 2012).

10 Non-reactive P is deposited at the sediment-water interface as detrital P, authigenic Ca-P, P bound to non-reactive Fe oxides (γ fraction) and P bound to non-reactive organic matter (γ fraction).

In the sediment, the rate of vivianite formation (R_{viv}) is modeled by means of Michaelis-Menten kinetics for dissolved Fe^{2+} and HPO_4^{2-} , which implies that the rate of vivianite formation depends on both porewater species and that there is a maximum rate of formation (Reed et al., 2016):

$$15 \quad R_{viv} = V_{max} \left(\frac{[\text{Fe}^{2+}]}{[\text{Fe}^{2+}] + K_{\text{Fe}^{2+}}} \right) \left(\frac{[\text{HPO}_4^{2-}]}{[\text{HPO}_4^{2-}] + K_{\text{HPO}_4^{2-}}} \right) \quad (2)$$

where V_{max} is the maximum rate ($\text{mol L}^{-1} \text{s}^{-1}$), $K_{\text{Fe}^{2+}}$ and $K_{\text{HPO}_4^{2-}}$ are the half saturation constants, $[\text{Fe}^{2+}]$ and $[\text{HPO}_4^{2-}]$ are the porewater concentrations of Fe^{2+} and HPO_4^{2-} .

3.4 Transient modeling scenario

The model was run to steady state for 200 years. Subsequently, temporal changes in the sedimentation rate and the input of organic matter, Fe oxides, Mn oxides and Mn carbonates were implemented to fit key porewater and solid phase depth profiles for site NB8 (Figs. 3 and S.4A-C). The modeled sedimentation rate in the first 200 years was set to 1 cm yr^{-1} ($0.34 \text{ g cm}^{-2} \text{ yr}^{-1}$), based on ^{210}Pb dating (Fig. S.2; Table 1). From 2003 onwards sedimentation was assumed to decrease to 0.6 cm yr^{-1} ($0.21 \text{ g cm}^{-2} \text{ yr}^{-1}$; Fig. 3A). The modeled organic matter deposition in the first 200 years was $7.65 \text{ mol m}^{-2} \text{ yr}^{-1}$. From 1987 to 2003, the deposition increased, whereas in the last 12 years the deposition decreased together with the sedimentation rate (Fig. 3B). Our modeled organic matter fluxes are at the high end of the range estimated for the region (1.1 to $8.2 \text{ mol m}^{-2} \text{ yr}^{-1}$; Algesten et al. (2006)). The qualitative trend in organic matter loading assumed in the model is in accordance with results from previous studies on eutrophication in the Bothnian Sea (Fleming-Lehtinen et al., 2008; Fleming-Lehtinen and Laamanen, 2012; Rooze et al., 2016).

The assumption is made that during strongly enhanced riverine Fe oxide input the P:Fe ratio of Fe oxides can be lower because on land the availability of HPO_4^{2-} is not high enough to maintain a high P:Fe ratio. This assumption is based on the dominance of natural forest and wetlands in the region (Björkvald et al., 2008). We note that the model results were very

sensitive to the P:Fe ratio and that we could not model the key profiles when assuming a higher P:Fe ratio. To be able to model a transient P:Fe ratio in the Fe oxide^β fraction a fifth Fe oxide fraction, Fe oxide^{β(pulse)}, was added to the model. This fraction has the same reactivity as Fe oxide^β towards organic matter and H₂S but has a P:Fe ratio of 0. By varying the ratio between Fe oxide^β and Fe oxide^{β(pulse)} the P:Fe ratio of the Fe oxide^β can be adjusted over time.

5 In the first 200 years, the Fe oxide input was set to 0.87 mol m⁻² yr⁻¹. The Fe oxide input was then assumed to increase from 1988 onwards until 1997 when a maximum in incoming Fe oxides was assumed, followed by a decrease in Fe oxide input (Figs. 3C). The strong pulse-type increase in Fe oxide input at this maximum was assumed to consist of mainly the β(pulse) fraction of Fe oxides (Fig. S.4B). Despite this lower P:Fe ratio, the total flux of P bound to Fe oxides was highest during this period of enhanced Fe oxide input (Fig. S.4D&E). The transient scenario of Fe oxide loading compares well to qualitative
10 trends used in a previous model study for the same region (Rooze et al., 2016). The initial Mn oxide flux was set to 0.085 mol m⁻² yr⁻¹ (Fig. 3D). In the last 17 years of the scenario, the Mn oxide flux was set to a much lower value. The input flux of Mn carbonate was always low compared to that of Mn oxides (4 - 29% of the total incoming Mn flux; Fig S.4C). Processes coupled to the presence of bioirrigating macrofauna (i.e. bioirrigation and the binding of P onto Fe oxides in the bioirrigated zone (R32 in Table S.2), were only implemented in the last 12 years of the run, from 2003 onwards.

15 A model sensitivity analysis was performed to investigate the impact of changes in bottom water salinity, the rate of sedimentation and input of organic matter and Fe oxides on P burial rates and forms. During these sensitivity analyses the transient baseline scenario was used (Fig. 3) and first one (initial) factor was varied per run. Salinity was varied over a range of 0 to 20. The sedimentation rate was varied from 0.25 to 2 cm yr⁻¹. The input of organic matter was varied between -70% and +25%; (3) input of Fe oxides was varied between -25% and +25% from the baseline scenario. Subsequently, a run was performed in
20 which the input of organic matter, Fe oxides and the sedimentation rate were all changed by the same factor as the sedimentation rate to account for the role of rivers as the main source of material in the region (Algesten et al., 2006; Björkvald et al., 2008).

4 Results

4.1 Porewater profiles

25 At all sites, depth profiles of porewater constituents showed relatively little difference between April and August 2015 (Fig. 4). Porewater SO₄²⁻ decreased with depth, with a distinct SMTZ only being present in the sampled depth interval at sites N7 and NB8 (Fig. 4). Concentrations of CH₄ were low at all other sites. Appreciable H₂S was only present at site NB8 in the SMTZ. Dissolved Fe²⁺ and Mn²⁺ profiles generally showed a maximum near the sediment-water interface and increased concentrations below ca. 5 to 25 cm depth in the sediment. Porewater profiles of NH₄⁺ and DIC increased with depth at all sites. Porewater
30 HPO₄²⁻ concentrations were low close to the sediment-water interface and increased with depth at all sites. At sites N7 and NB8, HPO₄²⁻ concentrations remained constant or decreased again below the SMTZ. Concentrations of Fe²⁺, Mn²⁺, NH₄⁺ and DIC, were highest at depth at site NB8 when compared to the other sites.

4.2 Solid phase profiles and sedimentation rate

Organic carbon contents in the surface sediment ranged between 2-4 wt% (Table 1) and decreased with depth at all sites (Fig. 5). Total S concentrations increased with depth in the upper 10 to 20 cm of the sediment and subsequently remained constant or varied with depth. Total P, total Mn, total Fe and Fe/Al were generally highest close to the sediment-water interface and decreased with depth at all sites except site NB8. Here, several subsurface enrichments in P and Mn were observed directly below maxima in total S, Fe and Fe/Al at depths of 21, 42 and 60 cm.

The Fe and P speciation for site NB8 reveals that the upper 10 cm of the sediment was strongly enriched in Fe oxides and Fe-bound P. Minima in both Fe oxides and Fe-bound P were found between depths of 10 and 20 cm followed by either constant (Fe oxides) or varying (Fe-bound P) concentrations at greater depth (Figs. 6 and S.5). Maxima in AVS coincided with maxima in total S, total Fe and Fe/Al (Figs. 5&6) and minima in total Mn and Fe-bound P. Concentrations of exchangeable P were highest close to the sediment-water interface but account for only ~2% of total P. Concentrations of detrital P and authigenic Ca-P showed little change with depth.

Sedimentation rates at our study sites varied between 0.225 and 1 cm yr⁻¹ (Table 1). Rates of P burial ranged from 0.026 to 0.145 mol m⁻² yr⁻¹ (Table 1). The rates of sedimentation and P burial were highest at site NB8.

15 4.3 SEM-EDS

Examination of sieved sediment fractions for site NB8 with a light microscope revealed the presence of transparent to light blue crystals in sediment intervals below the SMTZ (55–58 cm). Scanning electron micrographs of the sieved fractions revealed crystals with a similar shape to that of vivianite crystals found in Lake Ørn, Denmark (O’Connell et al., 2015) and the deepest part of the Bothnian Sea (site US5B; Egger et al. (2015a); Fig. 7A) at all sieved intervals below the SMTZ (34–36 cm, 49–52 cm and 55–58 cm). Quantitative analysis of the crystals with electron microprobe-EDS revealed an average Fe:P ratio of 3.3 mol mol⁻¹ and the presence of significant amounts of Mn, Mg, Si and Al (Fig. 7B; Table S.5). In samples analyzed above and within the SMTZ such crystals were not observed.

4.4 Model results

Modeled porewater and solid phase depth profiles for site NB8 capture the main trends in the measured profiles (Figs. 4, 5 and 6). We note that the model slightly underestimates the amount of Fe-bound P in the upper 15 cm of the sediment and overestimates organic-P. The observed variations in total S, total Mn and Fe-P below 30 cm depth in the sediment were not targeted with the model.

Depth integrated rates of P cycling in 2015 (Fig. 8) show that the release of HPO₄²⁻ from organic-P accounts for only 2.3% of the HPO₄²⁻ release to the porewater at site NB8. The main source of HPO₄²⁻ is the release from Fe oxides, with H₂S-driven reductive dissolution accounting for 61% of the HPO₄²⁻ release and dissolution coupled to organic matter degradation accounting for 28% (Fig. 8). In the model, most of the Fe oxide reduction involves the less reactive beta fraction and takes place in the upper 20 cm of the sediment (Fig. S.6; R14&R15).

Approximately 30% of the HPO_4^{2-} removal from the porewater takes place through release to the overlying water by bioirrigation and diffusion, with the former being the most important process. Binding of HPO_4^{2-} to Fe oxides accounts for 60% of the removal while 10% is precipitated as vivianite (Fig. 8). However, Fe oxides that are formed *in-situ* are not a permanent sink for HPO_4^{2-} as the majority is dissolved through reductive dissolution. Burial of P as vivianite accounts for 41% of the total P burial at site NB8 (Fig. 8). At depth, P bound to vivianite becomes more important compared to P bound to Fe oxides (Fig. S.7).

In the model, total P burial rates increased from 0.12 to $0.34 \text{ mol m}^{-2} \text{ yr}^{-1}$ upon a decrease in salinity from 20 to 0 (Fig. 9). Changes in salinity did not affect the burial rates of Ca-P, organic P and P associated with Fe oxides. In the latter case, this was because only the unreactive fraction of Fe oxides remained. The percentage of P buried as vivianite increased strongly with decreasing salinity.

In the model scenario in which changes in the rates of sedimentation and organic matter and Fe oxide input were coupled, the total P burial rate increased from 0.025 to $0.45 \text{ mol m}^{-2} \text{ yr}^{-1}$ when assuming sedimentation rates between 0.25 and 2 cm yr^{-1} (Fig. 9). At a sedimentation rate of 0.5 cm yr^{-1} , little P was buried in the form of vivianite. At higher sedimentation rates, formation of vivianite in the sediment increased and the total burial of P was enhanced. Model runs in which changes in the same factors were evaluated separately revealed that increasing the rate of sedimentation or Fe oxide input both enhance vivianite formation and burial of P (Fig. 10A and B). The response to an increase in the rate of sedimentation is non-linear, with the greatest increase in P burial between 0.5 and 0.85 cm yr^{-1} . For organic matter, the model runs reveal an optimum input rate beyond which P and vivianite burial rates decrease (Fig. 10C).

5 Discussion

5.1 Phosphorus burial in the Öre Estuary

Sediments in the coastal zone of the Bothnian Sea have been suggested to act as an efficient sink for P from rivers and the open sea based on budget calculations and an assumed average burial rate of P of $0.007 \text{ mol m}^{-2} \text{ yr}^{-1}$ (Asmala et al., 2017). We find substantially higher rates of P burial in the Öre estuary ranging from 0.026 to $0.145 \text{ mol m}^{-2} \text{ yr}^{-1}$ (Table 1). If our data are representative for the wider area, sediments in the coastal zone of the northern Baltic Sea may be an even more efficient sink for P than previously thought.

In their study, Asmala et al. (2017) identified a linear relationship between P burial and rates of sedimentation for a range of coastal systems around the Baltic Sea, but excluding the northern areas because of a lack of data (Fig. 9). Strikingly, our study sites in the Öre Estuary are characterized by a higher burial of P than predicted by this relationship. This particularly holds for site NB8. In the following, we will assess whether vivianite formation can play a role in explaining this enhanced P retention. As discussed in detail by (Egger et al., 2015a), vivianite formation is generally most pronounced in sediments below the SMTZ, where both Fe^{2+} and HPO_4^{2-} accumulate in the porewater due to dissolution of Fe oxides and release of associated P. While we find both solutes in the porewater at depth at all sites, the highest concentrations are observed at sites N7 and NB8 where a distinct SMTZ was present between ca. 10 and 20 cm depth in the sediment. The position of this SMTZ shows little

seasonality, likely because of the refractory nature of the sediment organic matter, which is mostly of terrestrial origin, and the relatively limited seasonal change in bottom water temperature. This implies that any vivianite formed below the SMTZ likely will be preserved and buried, because there will be no further exposure to sulfide.

Detailed analyses of the sediments at site NB8 with SEM-EDS confirm the presence of vivianite crystals below the SMTZ and a lack thereof in and above the SMTZ (Fig. 7). This trend with depth points toward an authigenic origin. The average Fe:P ratio of the crystals of 3.3 mol mol^{-1} (Table S.5) is higher than the 2:1 stoichiometric ratio of vivianite. Similar high ratios were also observed for vivianite crystals in sediments of the Landsort Deep in the Baltic Proper, where they were explained by surface enrichments of Fe (Dijkstra et al., 2016). The vivianite was also enriched in Mn and Mg, which are both elements that are known to be included in the structure of the mineral (Dijkstra et al., 2016, 2018; Egger et al., 2015a). The presence of Al and Si (Table S.5) likely reflects the presence of clay particles that were not removed prior to the SEM-EDS analysis (Egger et al., 2015a; Dijkstra et al., 2018).

The Fe-P below the SMTZ (Fig. 6) likely is a mixture of both Fe oxide bound P and vivianite, as shown previously for sediments in the deepest part of the Bothnian Sea (Egger et al., 2015a). Due to dissolution of Fe oxides and vivianite formation in the sediment the fraction of P bound to vivianite increases with depth (Fig. S.7). The results of the reactive transport model suggest that Fe oxide bound P and vivianite account for ca. 15% and 40% of the total burial of P, respectively. Authigenic Ca-P and organic P concentrations are relatively low and each account for ca. 15% of total P burial (Fig. S.5). The remainder of the P is buried as non-reactive P.

5.2 Vivianite formation in coastal sediments in the northern Baltic Sea

Vivianite formation in sediments strongly depends on the balance between the formation of H_2S and the input of Fe oxides (Ruttenberg, 2003). When there is an excess of Fe oxides over H_2S , not all Fe oxides will be converted to Fe sulfides, and more Fe^{2+} will be available to precipitate with HPO_4^{2-} as vivianite (Rozaan et al., 2002; Gächter and Müller, 2003; Hartzell et al., 2017). The results of the sensitivity analysis (Figs. 9 and 10) show that the bottom water salinity and input of Fe oxides play a critical role in controlling this balance, with vivianite formation and total P burial increasing strongly at lower salinities and with high Fe oxide inputs. A higher sedimentation rate also enhances the formation of vivianite and P burial because of more rapid burial of Fe oxides below the SMTZ. In our model scenario, sedimentation rates greater than 0.5 cm yr^{-1} were particularly conducive to vivianite formation. Vivianite formation is also highly sensitive to the input of organic matter. When the input of organic matter is lowered to -75% of that assumed in the baseline scenario, the release of Fe^{2+} to the porewater due to Fe oxide reduction decreases to such an extent that formation of vivianite is limited by the availability of Fe^{2+} . Consequently, P burial decreases. An increased input of organic matter relative to the baseline scenario enhances the formation of H_2S and leads to a decline in vivianite formation and P burial. When assuming that changes in the rate of sedimentation and the input of Fe oxides and organic matter are coupled (Fig. 9), the net effect is an increase in vivianite formation and P burial. In summary, conditions for vivianite formation are most favorable in sediments with a low bottom water salinity, a high sedimentation rate and a high input of Fe oxides. While high rates of organic matter input are also required, there is an optimum rate above which vivianite formation declines.

5.3 Variations in riverine Fe and organic matter fluxes

In the Bothnian Sea, boreal rivers are the main source of Fe and organic matter to the coastal zone (Algesten et al., 2006; Björkvald et al., 2008; Palviainen et al., 2015). The input from rivers can be highly variable between years (Rember and Trefry, 2004; Hölemann et al., 2005; Sarkkola et al., 2013). The variations in sediment Fe, S and Fe/Al with depth, with maxima at 5 depths of 21, 42 and 60 cm at site NB8, are in accordance with such a variation in input (Fig. 5). This is confirmed by the model, since a strong increase in input of Fe oxides and organic matter is required to describe the maxima in Fe and S in the SMTZ (Fig. 5) and the maximum in vivianite directly below it (Fig. 6). This increased input of Fe oxides and organic matter leads to enhanced conversion of Fe oxides to Fe sulfides. We suggest that these high inputs of Fe and organic matter are directly linked to variations in river discharge, that may be linked to negative phases in the North Atlantic Oscillation (Gillibrand et al., 10 2005). In 1996 a dry period affected the entire Bothnian Sea region (Fig. S.8; Marttila et al. (2016)). In that year, the Öre River discharge was unusually low (Fig. 2). In the following years, i.e. starting in 1997, this then led to an increased input of Fe downstream (Sarkkola et al., 2013). This timing coincides with the maximum in Fe and organic matter input assumed in our model scenario (Fig. 3). In the modeling study for the deep basin site in the Bothnian Sea the timing of the enhanced Fe input also corresponds to the year 1997 (Rooze et al., 2016), implying that a wide area was affected. Although not included in the 15 model, a similar scenario would explain the enrichments of Fe, S and Fe-bound P at greater depth in the sediment, with the 1976 dry period leading to enhanced input of Fe and organic matter starting in 1977 and the Fe enrichment at 42 cm depth. In contrast to Fe, limited re-oxidation of Mn is expected during a dry period because of less formation of reduced Mn species (Burdige, 1993). Therefore, no strong increase in riverine Mn input is expected after a dry period. In summary, our results show that variations in rainfall on land play a critical role in the transport of Fe and organic matter in rivers to the coastal zone. This 20 riverine transport ultimately determines how much P is buried in the coastal zone. In the coastal Bothnian Sea, P burial is twice as high as the input of P from land, implying that large amounts of the buried P are imported from the open sea (Asmala et al., 2017). Part of the P in the open sea is known to be imported from the adjacent eutrophic Baltic Proper (Savchuk, 2005). The high P burial in the coastal zone coupled to the input of Fe from rivers likely contributes to the seasonal P limitation observed in the Bothnian Sea (Tamminen and Andersen, 2007).

25 5.4 Implications

In most marine systems, the balance between H_2S formation and Fe oxide input is such that most Fe oxides are converted to Fe sulfides, thereby allowing only limited vivianite formation (Ruttenberg, 2003). Here we show, that in estuaries with high inputs of Fe oxides from rivers, high sedimentation rates and sufficient input of organic matter, this balance can become very favorable for the formation of vivianite. Such estuaries can act as a highly effective "coastal filter" for P from rivers and for P 30 imported from the open sea (Bouwman et al., 2013; Asmala et al., 2017).

Our study also highlights the role of bottom water salinity in vivianite formation. Because many studies focus on the relatively high salinity parts of estuaries (e.g. as compiled for the Baltic Sea in Asmala et al. (2017)), the role of vivianite as a sink for P has been largely overlooked.

Sea level rise is expected to increase bottom water salinity in coastal areas in future (Scavia et al., 2002). In the Baltic Sea, however, salinity is expected to decrease because of enhanced precipitation on land and associated higher river runoff (Graham, 2004; Meier et al., 2006). Recent studies also indicate that Fe^{2+} input from rivers in Europe and North America increased over the past few decades, possibly due to changes in land use and expanded forestry (Kritzberg and Ekström, 2012; Björnerås et al., 2017). For the coastal zone of the Baltic Sea, both a decline in salinity and a continued enhanced input of Fe from rivers will promote conditions for vivianite formation in the sediment and increase its role as a sink for P. Detailed studies of other coastal areas are required to allow a prediction of the role of vivianite formation in the global coastal ocean, since an increased salinity and increased Fe input have opposite effects on the formation of vivianite.

6 Conclusions

Our study reveals a very high burial of phosphorus (P) in sediments of an oligotrophic estuary in the northern Bothnian Sea (up to $0.145 \text{ mol P m}^{-2} \text{ yr}^{-1}$). These sediments act as a highly efficient sink for P from rivers and the open sea. We demonstrate that the high P retention in the sediment is related to the formation of vivianite, which is visible in the form of discrete crystals below the sulfate methane transition zone at the site with the highest sedimentation rate. By combining P extractions and reactive transport modeling of solid phase and porewater profiles, we demonstrate that vivianite accounts for 40% of total P burial at the same site. With the model, we also assess the sensitivity of vivianite formation to the key drivers of variations in the availability of H_2S versus Fe oxides. We show that vivianite formation is promoted when bottom water salinity is low and rates of sedimentation and inputs of Fe oxides are high. High organic matter inputs are also a requirement, but in our scenario, there is a distinct optimum for vivianite formation.

We suggest that enrichments of Fe, S and P in the sediment are linked to periods of enhanced riverine input of Fe and organic matter. Two sets of enrichments can be coupled to the years 1977 and 1997, when riverine fluxes of Fe were likely enhanced in a period following a dry year on land in 1976 and 1996, respectively. The enhanced input of Fe and organic matter likely increased the formation of vivianite and the burial of P in the sediment.

In the future, climate change is expected to enhance the freshwater input to the Baltic Sea and thereby decrease its salinity. Continued elevated Fe^{2+} input from rivers is also expected. Both, a decreasing salinity and an increased Fe input will create more favorable conditions for vivianite formation in the sediment. We therefore expect that, in future, vivianite will become more important as a sink for P in the coastal zone of the Baltic Sea.

Data availability. All data will be made available in the database Pangea upon acceptance of the manuscript.

Code and data availability. The model code is available from WL and CS upon request.

Author contributions. CS, WL, NH and DC designed the research. WL, ME, NH and DC performed the analyses. WL performed the model simulations. WL, ME, NH, EK and CS interpreted the data. WL and CS wrote the paper with comments provided by ME, NH, EK and DC.

Competing interests. The authors declare that they have no conflict of interest.

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Figures

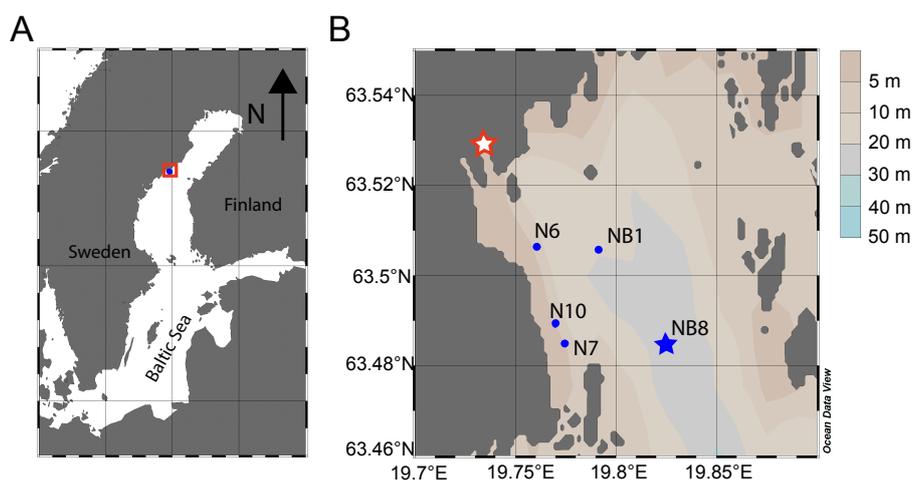


Fig. 1. A. The Öre Estuary on the Swedish coast in the Bothnian Sea; B. Locations of the five sampling sites. Site NB8, in the deepest part of the estuary, is indicated with a blue star. The mouth of the Öre River is indicated with a red star. Figure drawn using Ocean Data View (Schlitzer, 2015).

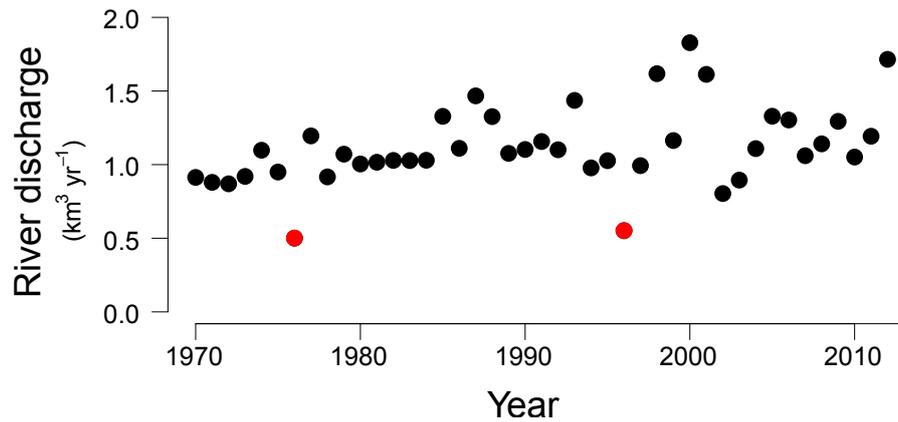


Fig. 2. Öre River discharge ($\text{km}^3 \text{yr}^{-1}$) from 1970-2012 (Swedish Meteorological and Hydrological Institute (www.SMHI.se)). The red dots indicate two years with an unusually low river run-off, 1976 and 1996, respectively.

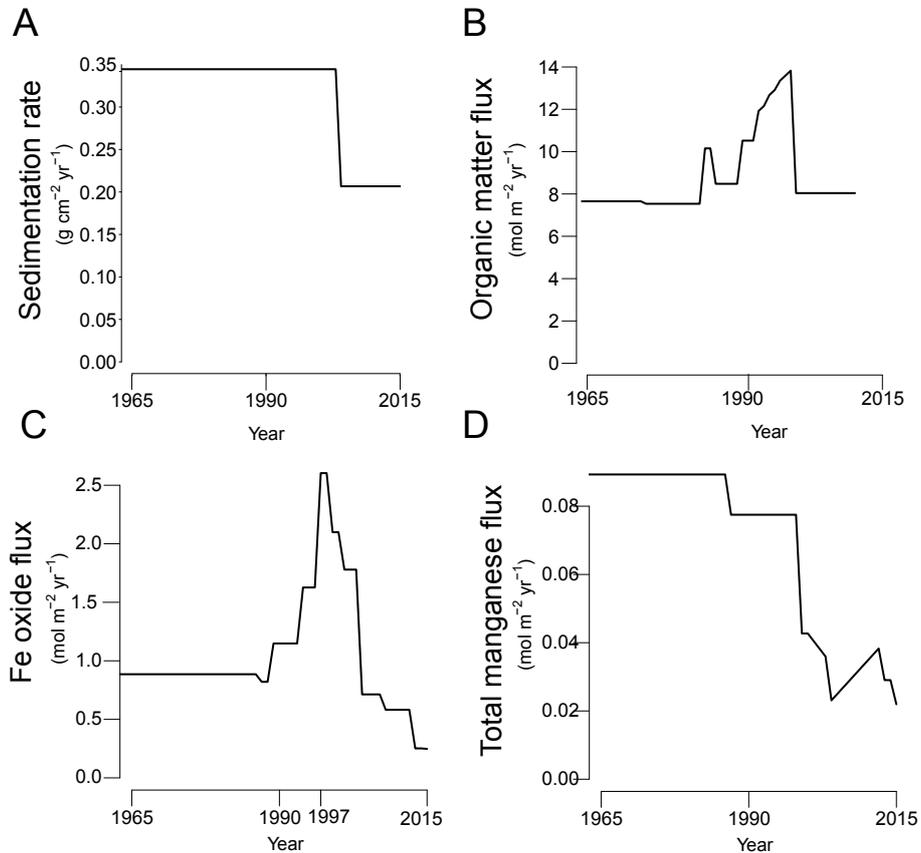


Fig. 3. Transient fluxes at the sediment-water interface from 1965-2015 as used in the reactive transport model; A. sedimentation rate; B. organic matter input; C. Fe oxide input. D. total Mn input (Mn oxide and Mn carbonate). Partitioning of different phases of organic matter, Fe oxides and manganese are shown in figure S.4A-C

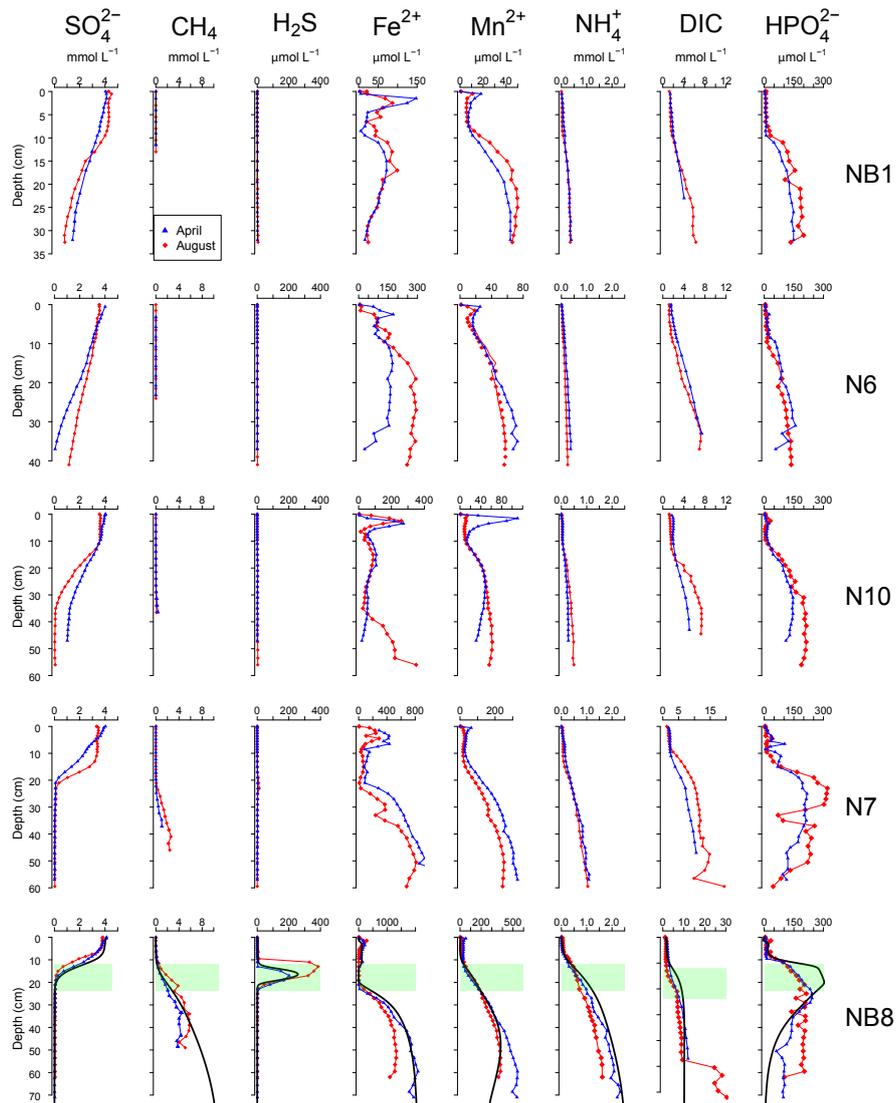


Fig. 4. Porewater depth profiles of SO_4^{2-} , CH_4 , H_2S , Fe^{2+} and Mn^{2+} , NH_4^+ , DIC and HPO_4^{2-} for sites NB1, N6, N10, N7 and NB8 in April (blue) and August (red) 2015. Porewater profiles of station NB8 include model fits to the April 2015 data for the baseline scenario (black lines). The SMTZ at site NB8 is indicated by the green shaded area.

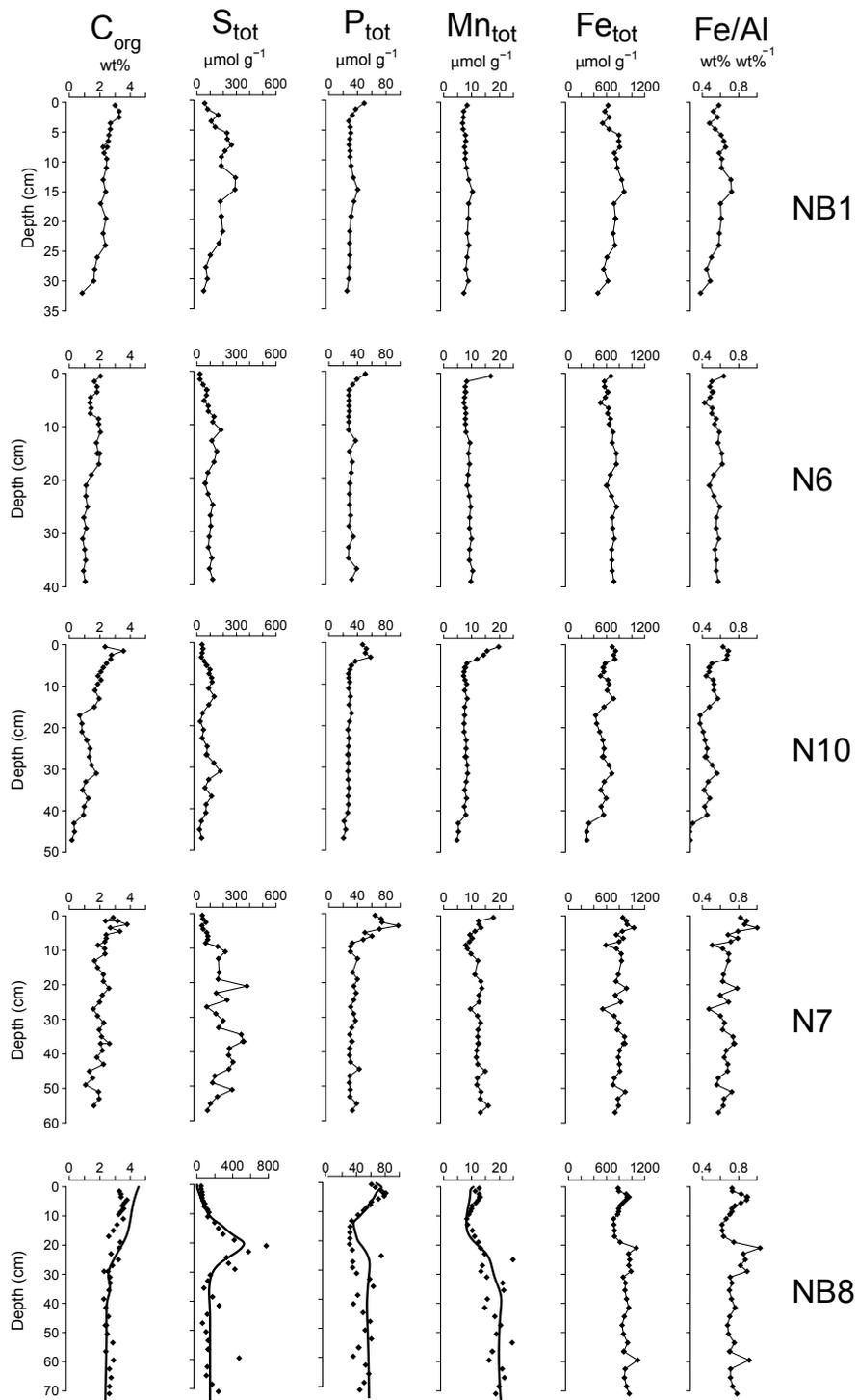


Fig. 5. Solid phase depth profiles of organic carbon, total S, total P, total Mn, total Fe and Fe/Al for sites NB1, N6, N10, N7 and NB8 in April 2015. Solid phase profiles of station NB8 include model fits to all profiles (black lines) except total Fe and Fe/Al for the baseline scenario.

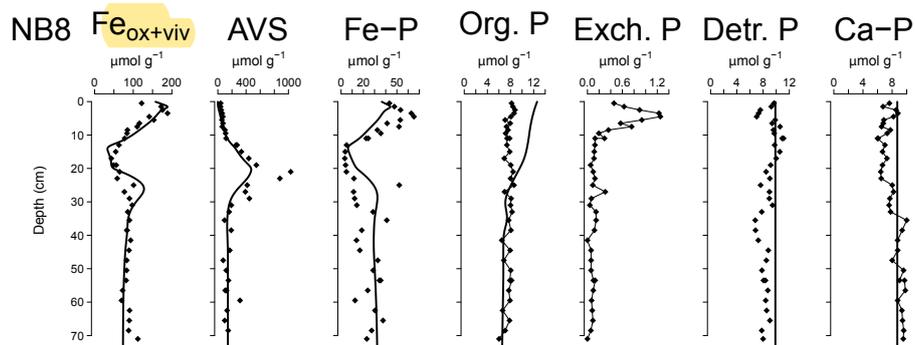


Fig. 6. Solid phase depth profiles of Fe oxides, Fe-bound P (Fe-P), AVS, organic-P (Org. P), exchangeable P (Exch. P), detrital Ca-P (Detr. P) and authigenic Ca-P (Ca-P) for site NB8 in April 2015. Solid phase profiles include model fits of the baseline scenario for all profiles except exchangeable P (black lines).

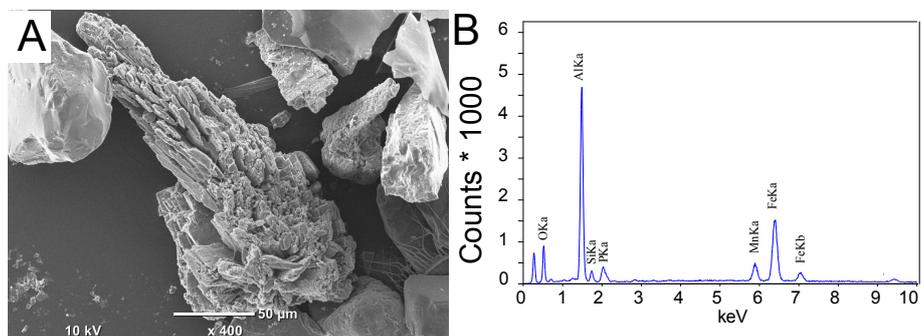


Fig. 7. A: Scanning Electron Micrograph (SEM): example of a vivianite crystal from the 34-36 cm depth interval at site NB8 sampled in August 2015. B: Electron microprobe-EDS spectrum of a spot measurement on the surface of the vivianite crystal.

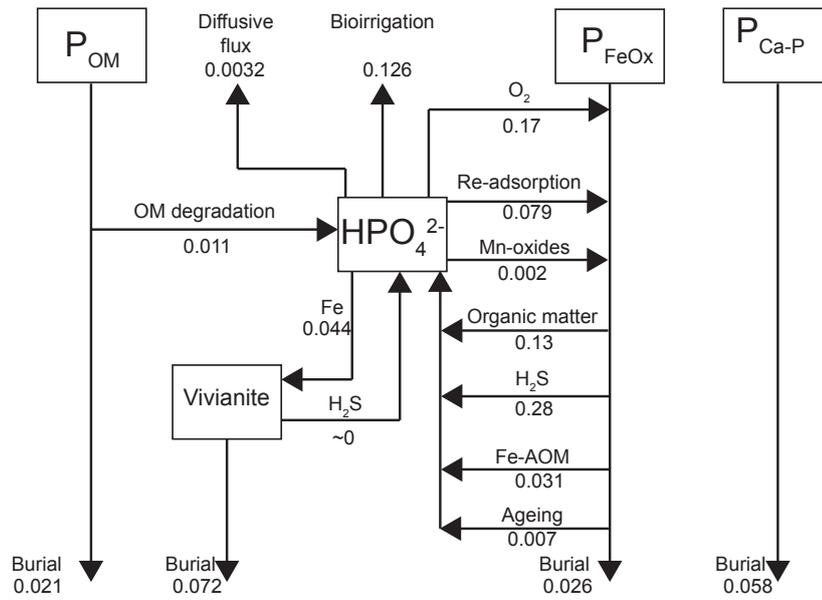


Fig. 8. Mass balance of P as calculated with the transient reactive transport model for 2015 (Fig. 3). Results are in non-steady state. Fluxes are in $\text{mol P m}^{-2} \text{yr}^{-1}$.

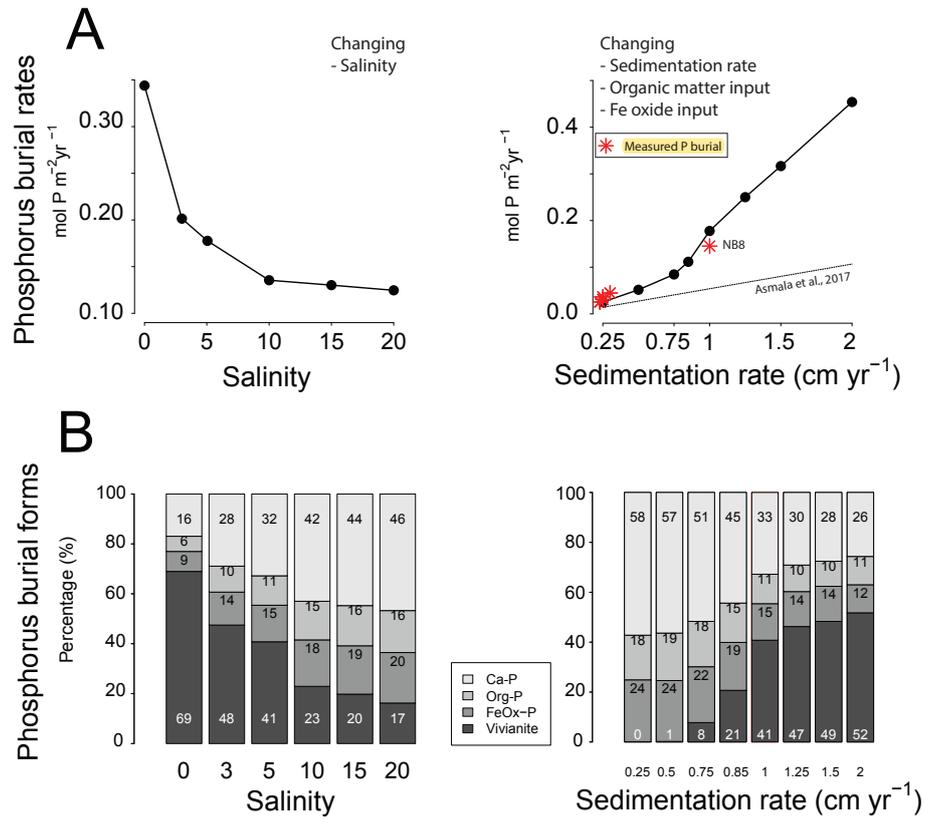


Fig. 9. Sensitivity of A. total phosphorus burial rate and B. the burial forms of P at site NB8 to changes in salinity, as well as in sedimentation rate and inputs of organic matter and Fe oxides as calculated in the model. Four burial forms of P are distinguished: authigenic and detrital apatite (Ca-P), organic-P (Org P), P bound to Fe oxides (FeOx-P) and vivianite. The dashed line indicates the total P burial as a function of sedimentation rate in the coastal zone of the Baltic Sea as suggested in Asmala et al. (2017). Red stars are the burial rates of P as measured at our five sites (Table 1). Sedimentation rates are initial sedimentation rates at t=0.

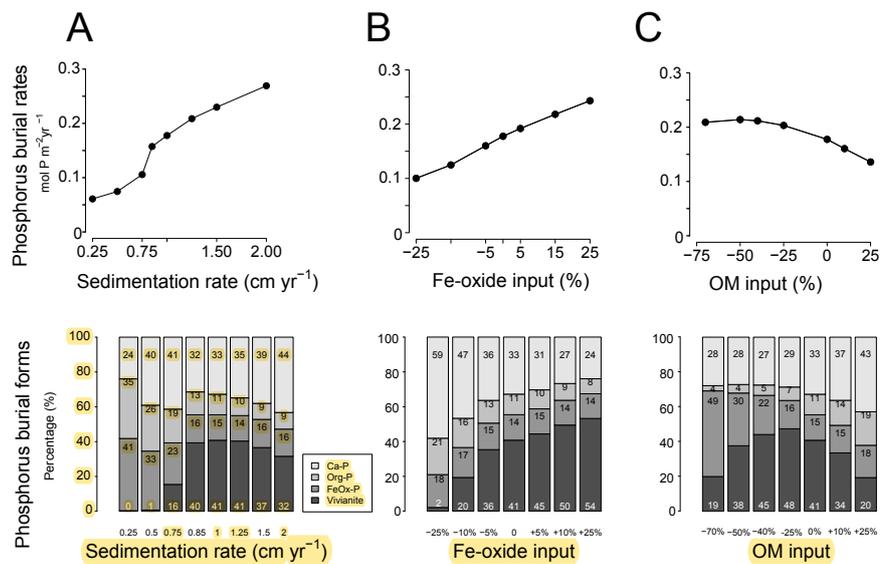


Fig. 10. Sensitivity analysis of P burial as a function of A: changing sedimentation rate between 0.25 and 2 cm yr⁻¹ and burial forms of P; B: organic matter input ranging between -70% and +25% and burial forms of P; C: changing input of Fe oxides ranging between -25% and 25% and burial forms of P.

Table 1. Water depth, temperature, coordinates and organic carbon at five sites sampled in the Öre Estuary in April and August 2015. Depth unit mbss is meters below sea surface. Bottom water temperatures were derived from CTD data. Total organic carbon (C_{org}) is given as the average for the top 2 cm ($n=2$), with standard deviation between parentheses. Sedimentation rates for sites NB1, N6, N10 and N7 were determined on cores collected in April 2015. The sedimentation rate at site NB8 was determined on a core collected in August 2015.

Site	Water depth mbss	Temperature °C (Apr/Aug)	Latitude °N	Longitude °E	C_{org} wt. %	Sed. rate cm yr ⁻¹	P burial mol m ⁻² yr ⁻¹
NB1	10	2.8 / 7.2	63.304	19.475	3.58(±0.14)	0.225	0.026
N6	17.2	3.2 / 15.2	63.303	19.454	2.06(±0.25)	0.3	0.044
N10	20.8	2.9 / 7.8	63.293	19.462	3.40±(0.70)	0.25	0.037
N7	18.8	2.8 / 9.8	63.291	19.465	3.14(±0.30)	0.25	0.031
NB8	33.2	2.8 / 6.3	63.291	19.495	3.85(±0.07)	1	0.145

Tables Paper

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1 Supplements

1.1 Detailed model description

The reactions in the reactive transport model describe organic matter degradation coupled to different electron acceptors. Reactions are divided in primary redox reactions and other biogeochemical reactions (Table S.6). The succession of oxidants during organic matter degradation (Froelich et al., 1979) is described by means of Monod kinetics (Table S.2; Boudreau (1997)). This means that the oxidants with the highest metabolic free energy yield are preferentially used until they become limiting and the oxidant with the next highest energy yield is used (Berg et al., 2003; Boudreau, 1996a; Wang and Van Cappellen, 1996). Respiratory reactions occur where O_2 , NO_3^- , $Mn(OH)_2$, $Fe(OH)_3$ and SO_4^{2-} serve as electron acceptors and finally organic matter is subject to methanogenesis (Reed et al. (2011a, b); Rooze et al. (2016); Table S.2). Organic matter includes carbon (C), nitrogen (N) and P in a C:N:P ratio of 106:16:0.35. In the model, oxidation of CH_4 is possible with O_2 , $Mn(OH)_2$, $Fe(OH)_3$ and SO_4^{2-} . Dissolved inorganic carbon in the model is calculated as the sum of the carbon in CO_2 and HCO_3^{2-} , which is produced or consumed by modeled reactions (Table S.6).

The generic mass conservation equations for solids and solutes are described by Eq. 1 and 2;

$$(1 - \phi) \frac{\partial C_s}{\partial t} = -(1 - \phi)v \frac{\partial C_s}{\partial z} + \sum R_s \quad (1)$$

$$15 \quad \phi \frac{\partial C_{aq}}{\partial t} = \phi D' \frac{\partial^2 C_{aq}}{\partial z^2} - \phi u \frac{\partial C_{aq}}{\partial z} + \sum R_{aq} \quad (2)$$

$$D' = \frac{D_m}{1 - \ln \phi^2} \quad (3)$$

where C_s is the concentration of solid species (mol L^{-1}), C_{aq} is the concentration of dissolved species (mol L^{-1}), t is time (yr), ϕ is the sediment porosity, v and u are the advective velocities of solid and dissolved species (cm yr^{-1}), respectively. Variables v and u were described by a depth-dependent function to account for changes in porosity (Meysman et al., 2005). Distance from the sediment-water interface is z (cm), D' the diffusion coefficient of dissolved species ($\text{cm}^2 \text{yr}^{-1}$), corrected for tortuosity in the porous medium ((Boudreau, 1996b), Eq. 3). $\sum R_s$ and $\sum R_{aq}$ are the net reaction rates from the chemical reaction (Table S.2) for solid and dissolved species.

Porosity (ϕ) is described by Eq. 4 to account for sediment compaction (Meysman et al., 2005; Reed et al., 2011b),

$$\phi(x) = \phi_\infty + (\phi_0 - \phi_\infty) e^{-\frac{x}{y}} \quad (4)$$

where ϕ_0 is the porosity at the sediment-water interface, ϕ_∞ is the porosity at depth and y is the porosity attenuation factor/e-folding distance (Fig. S.3A, Table S.3). The model code was written in R with the use of the marelac geochemical dataset package (Soetaert et al., 2010). To calculate the transport in porous media, the R package Reactran was used (Soetaert and Meysman, 2012). The set of ordinary differential equations was solved numerically with the Lsode integrator algorithm (Petzold, 1983).

Zero gradient boundary conditions were applied to the base of the model domain for all chemical species. To avoid influence of the boundary conditions at the base of the model domain results, the total depth of the model was set to 90 cm (divided into 900 grid cells of 0.1 cm).

Reaction parameters were mostly taken from literature or obtained within existing parameter ranges (Table S.7). If these were not available, or no fit to the data could be obtained with existing ranges, parameters were constrained by fitting the model to the measured data. The large number of model components, the parameters specific for the field site and the reaction kinetics

and parameters from the literature greatly limit the degrees of freedom while fitting the model to the data (Van Cappellen and Wang, 1996).

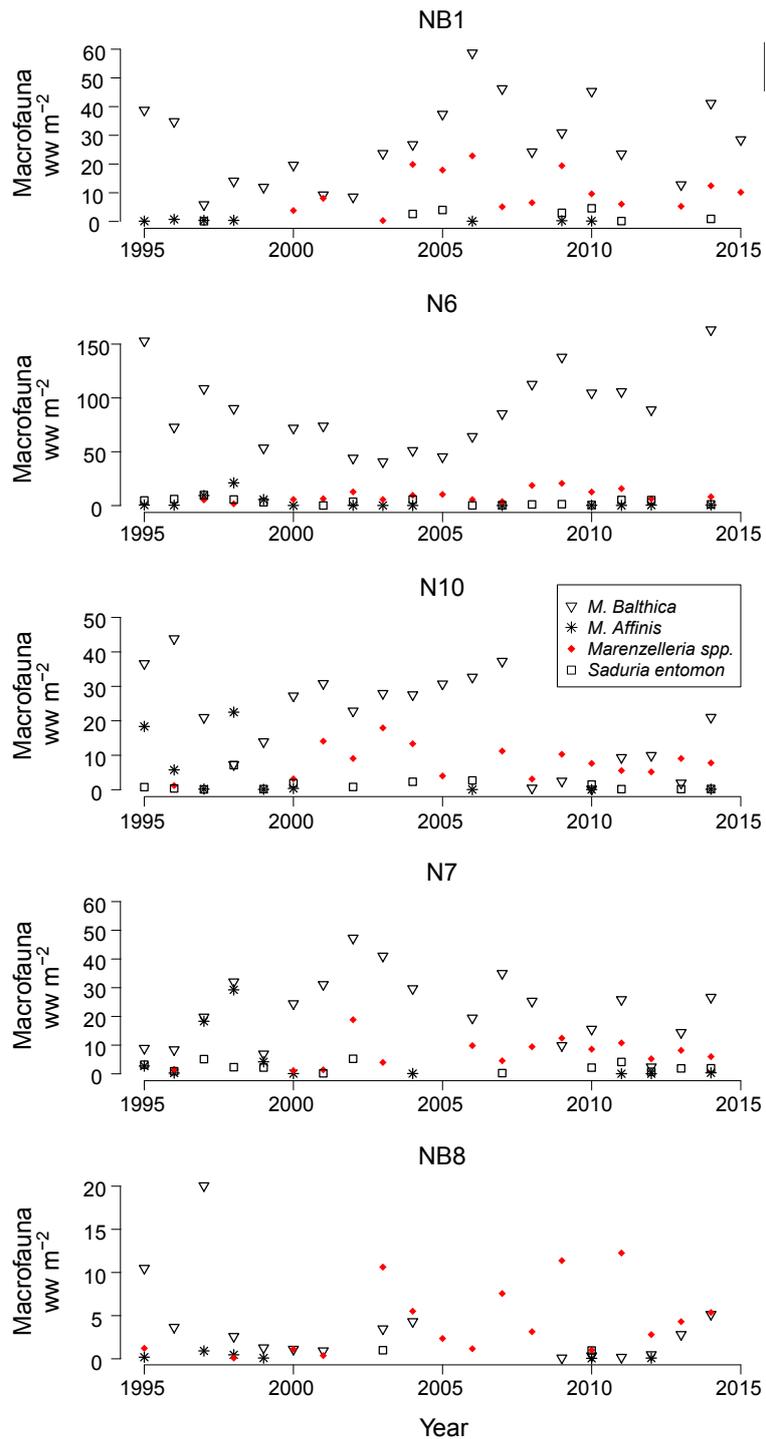


Figure S.1. Wet weight of macrofauna (ww m^{-2} ; in grams) at sites NB1, N6, N10, N7 and NB8 in the Öre Estuary from 1995-2015 (www.SMHI.se).

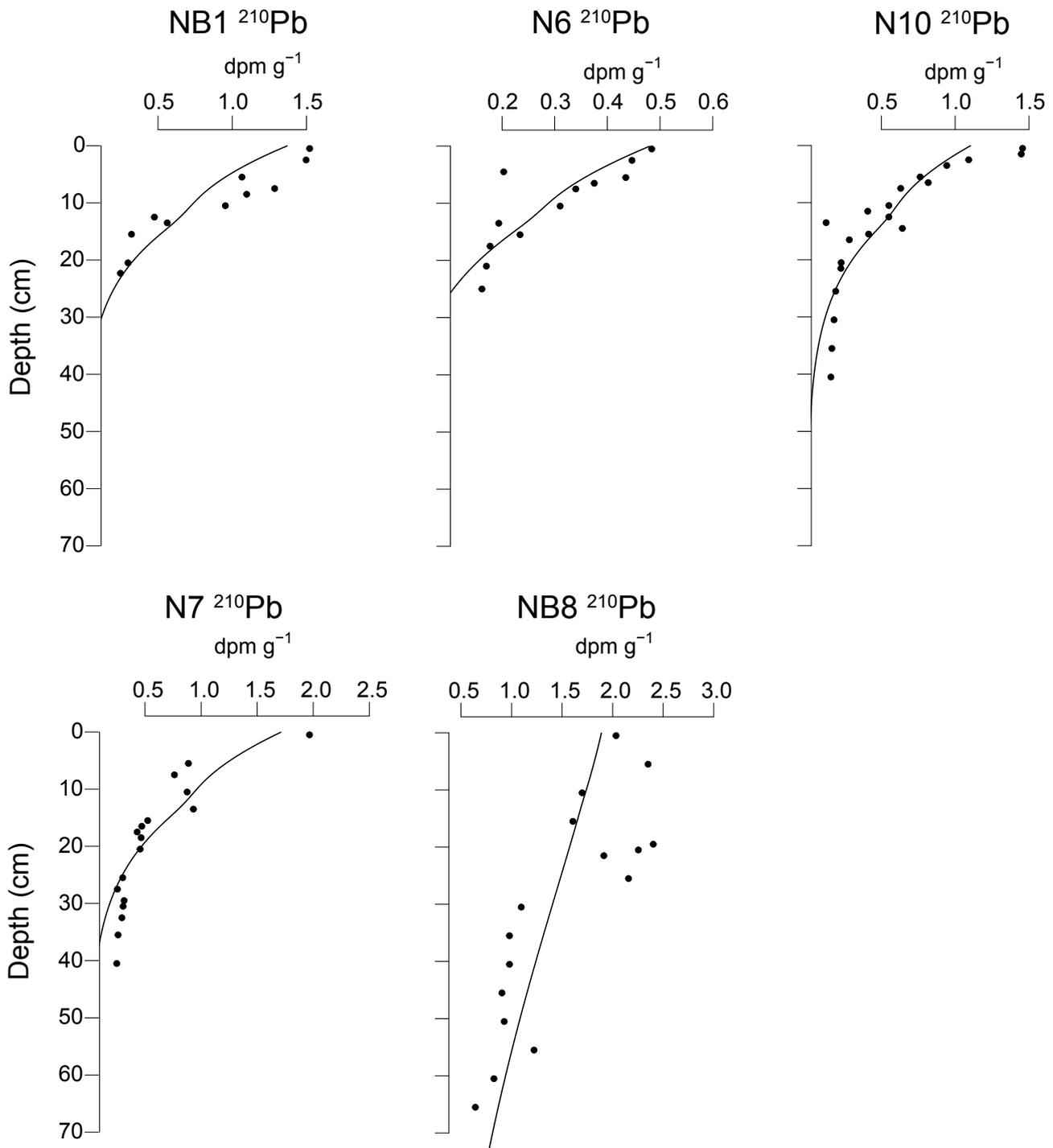


Figure S.2. Solid phase depth profiles of ^{210}Pb at sites NB1, N6, N10, N7 and NB8 and model fits (black lines). Sites NB1, N6, N10 and N7 were sampled in April 2015. Site NB8 was sampled in August 2015.

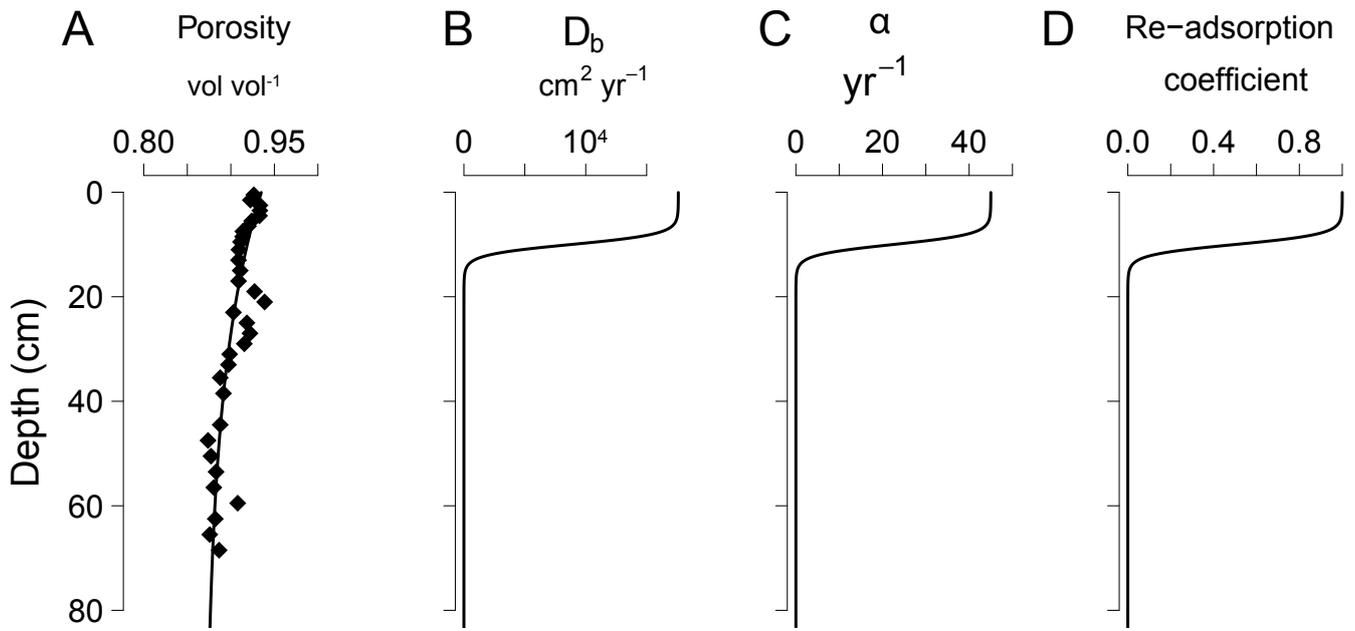


Figure S.3. Depth profiles used in the model A: Measured porosity (vol vol⁻¹) for April 2015 (black circles) and fitted porosity (black line); B: bioturbation coefficient (D_b ; cm yr⁻¹); C: bioirrigation coefficient (α ; yr⁻¹); D: Re-adsorption coefficient for HPO₄²⁻.

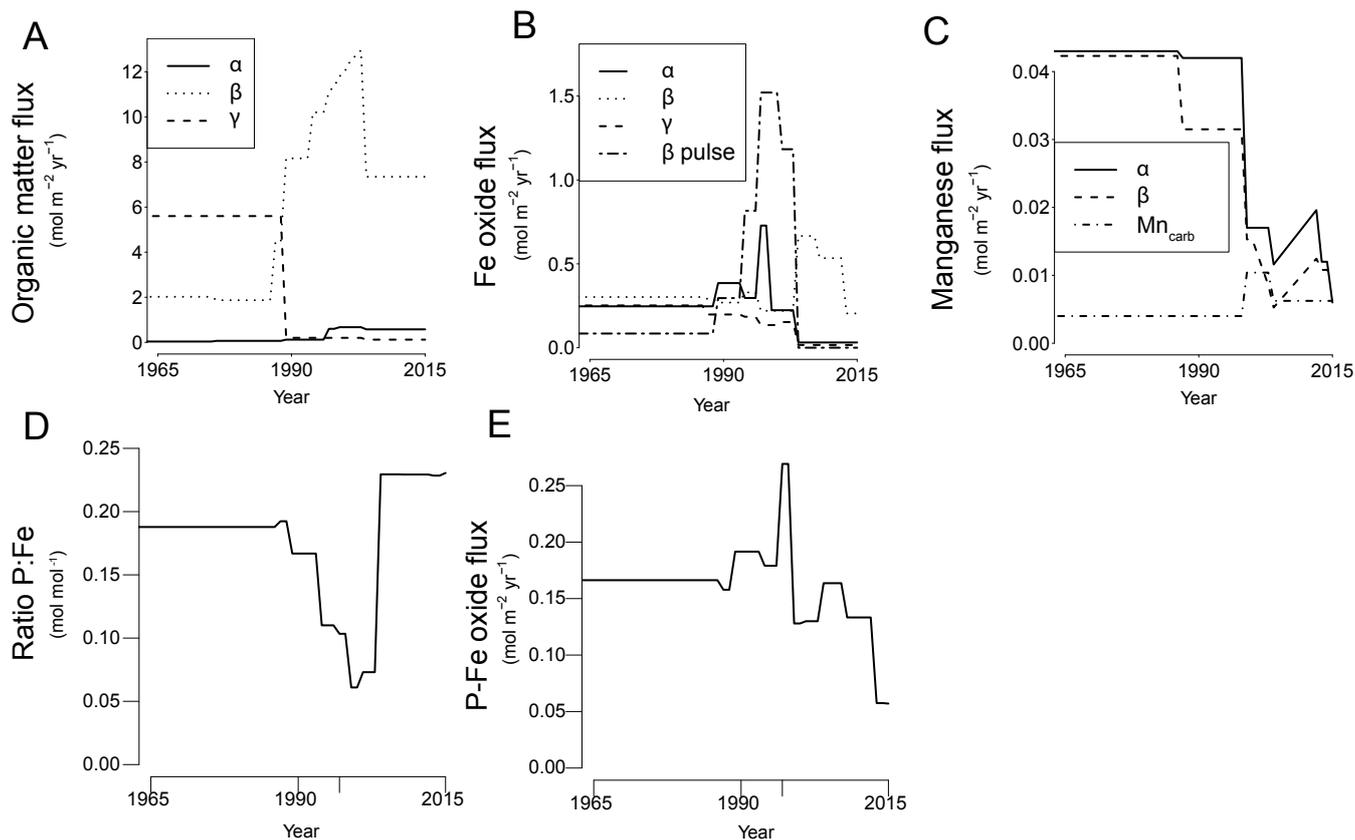


Figure S.4. Transient scenarios used in the reactive transport model between 1965 and 2015; A: different phases of organic matter; B different phases of Fe oxides; C: different phases of manganese; D: average P:Fe ratio of all Fe oxide fractions combined, E: total P input bound to Fe oxides. The various types of organic matter, Fe oxides and Mn oxides are indicated as α (highly reactive), β (less reactive) and γ (refractory).

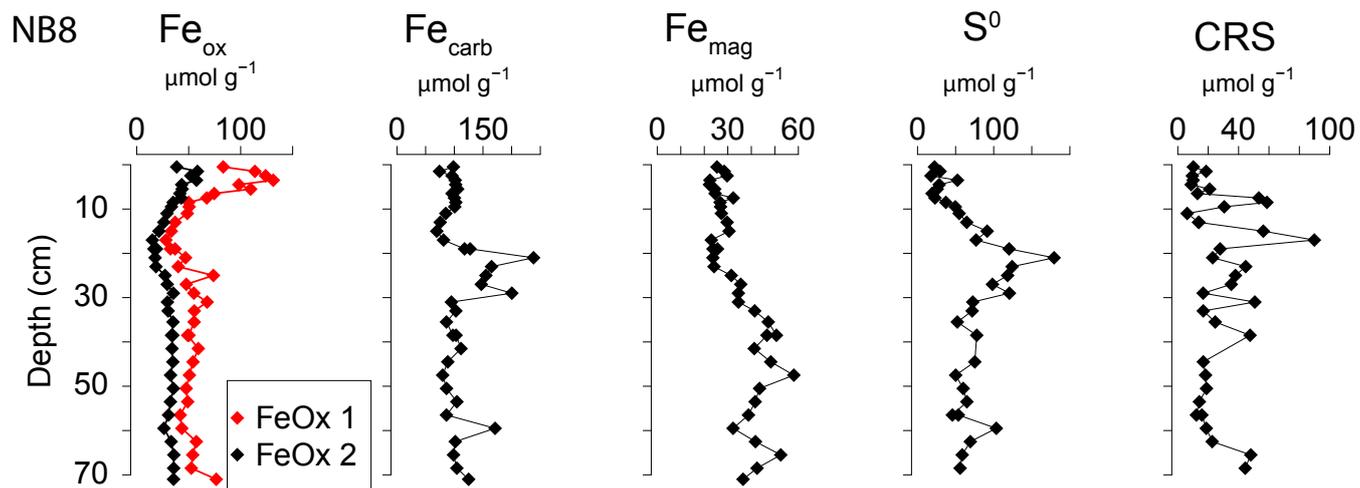


Figure S.5. Solid phase depth profiles of the easily reducible Fe oxides ($\text{Fe}_{\text{ox}1}$) and reducible (crystalline) Fe oxides ($\text{Fe}_{\text{ox}2}$) including vivianite, Fe carbonates (Fe_{carb}), magnetite (Fe_{mag}), elemental S (S^0) and S in pyrite (CRS) for site NB8 in April 2015.

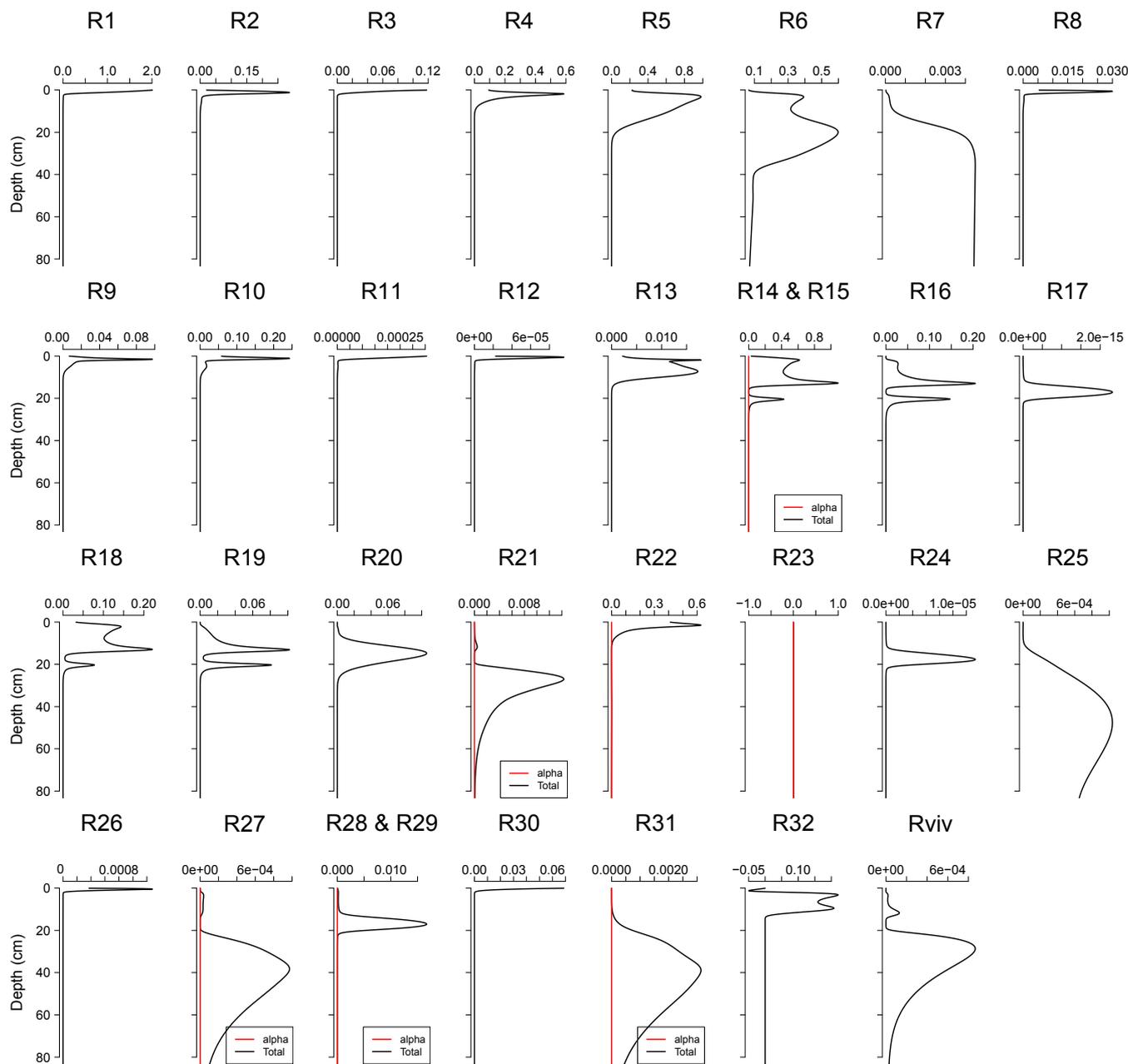


Figure S.6. Depth profiles of reaction rates calculated for the baseline scenario in 2015. Rates are in $\text{mol m}^{-3} \text{yr}^{-1}$. Reactions are described in Table S.6.

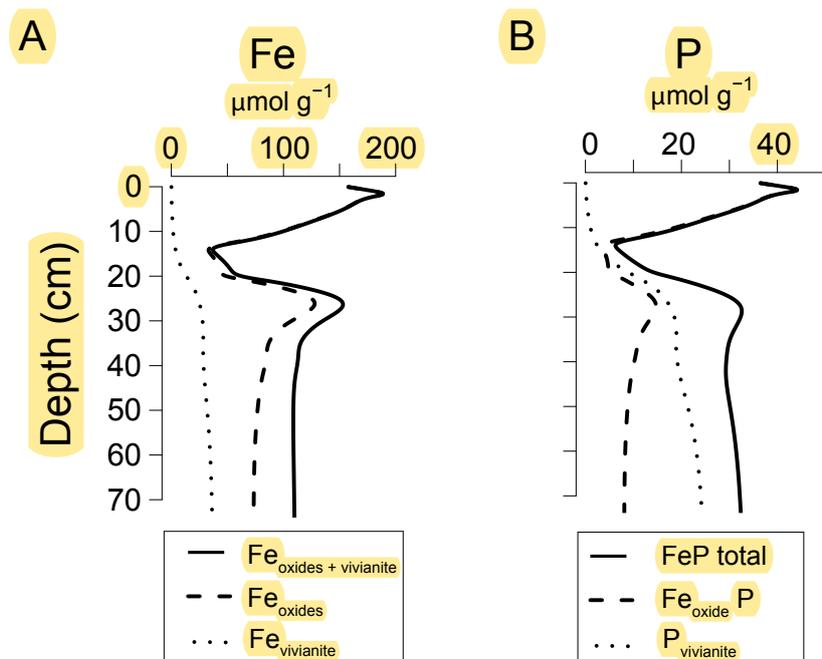


Figure S.7. Solid phase depth profiles of A: Fe bound to Fe oxides and vivianite; B: P bound to Fe oxides and vivianite.

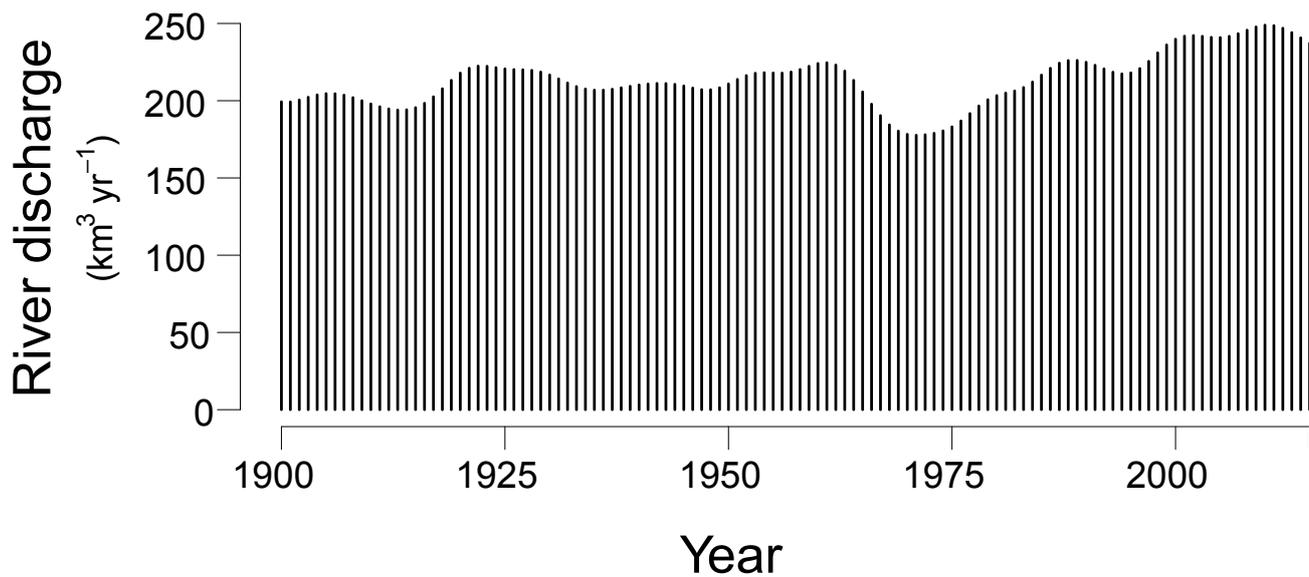


Figure S.8. Averaged summer river discharge for 86 Swedish rivers from 1900-2015 (www.SMHI.se).

Table S.1. Chemical species included in the model.

Species	Notation
Solid	
Organic matter ^a	OM ^{α, β, γ}
Iron oxide ^a	Fe(OH) ₃ ^{α, β}
Elemental sulfur	S ⁰
Iron monosulfide	FeS
Pyrite	FeS ₂
Iron-bound Phosphorus	Fe(OH) ₃ P
Vivianite	Fe ₃ (PO ₄) ₂
Siderite	FeCO ₃
Organic phosphorus	P _{org}
Authigenic (Ca) phosphorus	CaP
Detrital phosphorus	DetrP
Manganese oxide ^b	Mn(OH) ₂ ^{α, β}
Manganese carbonate	MnCO ₃
Solute	
Chloride	Cl ⁻
Oxygen	O ₂
Nitrate	NO ₃ ⁻
Sulfate	SO ₄ ²⁻
Methane	CH ₄
Iron	Fe ²⁺
Ammonium ^c	\sum NH ₄ ⁺
Hydrogen sulfide ^c	\sum H ₂ S
Phosphate ^c	\sum HPO ₄ ²⁻
Dissolved Inorganic Carbon	DIC
Manganese	Mn ²⁺

^a chemical species consist of 3 types: reactive (α), less reactive (β) and refractory (γ). Fe oxide ^{$\beta(pulse)$} and Fe oxide ^{$\beta(max)$} are not specifically named because they have the same characteristics as Fe oxide ^{β} .

^b chemical species consist of two types: reactive (α) and less reactive (β).

^c \sum denotes that all species of an acid are included.

Table S.2. Reaction pathways and stoichiometries implemented in the model.

Primary redox reactions	
$OM^{\alpha,\beta} + aO_2 \rightarrow aCO_2 + bNH_4^+ + cH_3PO_4 + aH_2O$	R1
$OM^{\alpha,\beta} + 0.8aNO_3^- + 0.8aH^+ \rightarrow aCO_2 + bNH_4^+ + cH_3PO_4 + 0.4aN_2 + 1.4aH_2O$	R2
$OM^{\alpha,\beta} + 2aMn(OH)_2^\alpha + 2aH^+ \rightarrow 2Mn^{2+} + aCO_2 + cH_3PO_4 + 2aH_2O$	R3
$OM^{\alpha,\beta} + 4aFe(OH)_3^\alpha + 4a\chi^\alpha Fe_{ox}P + 12aH^+ \rightarrow aCO_2 + bNH_4^+ + (c+4a\chi^\alpha)H_3PO_4 + 13aH_2O + 4aFe_2^+$	R4
$OM^{\alpha,\beta} + 0.5aSO_4^{2-} + aH^+ \rightarrow aCO_2 + bNH_4^+ + cH_3PO_4 + 0.5aH_2S + aH_2O$	R5
$OM^{\alpha,\beta} \rightarrow 0.5aCO_2 + bNH_4^+ + cH_3PO_4 + 0.5aCH_4$	R6
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	R7
Secondary and other reactions	
$2O_2 + NH_4^+ + 2HCO_3^- \rightarrow NO_3^- + 2CO_2 + 3H_2O$	R8
$O_2 + 4Fe^{2+} + 8HCO_3^- + 2H_2O + 4\chi^\alpha H_2PO_4^- \rightarrow 4Fe(OH)_3^\alpha + 4\chi^\alpha Fe_{ox}P + 8CO_2$	R9
$2O_2 + FeS \rightarrow SO_4^{2-} + Fe^{2+}$	R10
$7O_2 + 2FeS_2 + 2H_2O \rightarrow 4SO_4^{2-} + 2Fe^{2+} + 4H^+$	R11
$2O_2 + H_2S + 2HCO_3^- \rightarrow SO_4^{2-} + 2CO_2 + 2H_2O$	R12
$2O_2 + CH_4 \rightarrow CO_2 + 2H_2O$	R13
$2Fe(OH)_3^\alpha + 2\chi^\alpha Fe_{ox}P + H_2S + 4CO_2 \rightarrow 2Fe^{2+} + 2\chi^\alpha H_2PO_4^- + S^0 + 4HCO_3^- + 2H_2O$	R14
$2Fe(OH)_3^{\beta,\beta(max),\beta(pulse)} + 2\chi^\alpha Fe_{ox}P + H_2S + 4CO_2 \rightarrow 2Fe^{2+} + 2\chi^\alpha H_2PO_4^- + S^0 + 4HCO_3^- + 2H_2O$	R15
$Fe^{2+} + H_2S \rightarrow FeS + 2H^+$	R16
$FeS + H_2S \rightarrow FeS_2 + H_2$	R17
$4S_0 + 4H_2O \rightarrow 3H_2S + SO_4^{2-} + 2H^+$	R18
$FeS + S^0 \rightarrow FeS_2$	R19
$SO_4^{2-} + CH_4 + CO_2 \rightarrow 2HCO_3^- + H_2S$	R20
$CH_4 + 8Fe(OH)_3^{\alpha,\beta,\beta(max),\beta(pulse)} + 8\chi^{\alpha,\beta} Fe_{ox}P + 15H^+ \rightarrow HCO_3^- + 8Fe^{2+} + 8\chi^{\alpha,\beta} H_2PO_4^- + 21H_2O$	R21
$Fe(OH)_3^\alpha + (\chi^\alpha - \chi^\beta)Fe_{ox}P \rightarrow Fe(OH)_3^\beta + (\chi^\alpha - \chi^\beta)H_2PO_4^-$	R22
$Fe^{2+} + CO_3^{2-} \rightarrow FeCO_3$	R23
$Fe(PO_4)_2 + 3H_2S \rightarrow 2FeS + 2HPO_4^{2-} + 4H^+$	R24
$Mn^{2+} + HCO_3^- + OH^- \rightarrow MnCO_3 + H_2O$	R25
$2Mn^{2+} + 2O_2 + 4H^+ \rightarrow 2Mn(OH)_2^\alpha$	R26
$Mn(OH)_2^{\alpha,\beta} + 2H_3PO_4 + 2Fe^{2+} \rightarrow Mn^{2+} + 2\chi^\alpha Fe_{ox}P$	R27
$Mn(OH)_2^\alpha + H_2S \rightarrow Mn^{2+} + S_0 + 2H_2O$	R28
$Mn(OH)_2^\beta + H_2S \rightarrow Mn^{2+} + S_0 + 2H_2O$	R29
$Mn(OH)_2^\alpha \rightarrow Mn(OH)_2^\beta$	R30
$4Mn(OH)_2^{\alpha,\beta} + CH_4 + 7H^+ \rightarrow 4Mn^{2+} + HCO_3^- + 5H_2O$	R31
$Fe(OH)_3^{\beta,\beta(pulse)} + (\chi^{\beta(max)} - \chi^{\beta(pulse)})HPO_4^{2-} \rightarrow Fe(OH)_3^{\beta(max)}$	R32
Organic matter is of the form $((CH_2O)_a(NH_4^+)_b(H_3PO_4)_c)$, where $a=1$, $b=1/16$ and $c=300/1$. α , β , & γ describe different fractions (i.e. highly reactive, less reactive and refractory). $\chi^{\alpha,\beta,\gamma}$ describes the different P:Fe ratios of $Fe(OH)_3^{\alpha,\beta,\gamma}$. Reactions for different $Fe(OH)_3^\beta$ fractions (β , $\beta(max)$ and $\beta(pulse)$) are the same and are therefore combined as $Fe(OH)_3^\beta$.	

Table S.3. Environmental parameters used in the model.

Description	Symbol	Value or expression	unit	source
Porosity at the Surface	ϕ_0	0.935	vol vol ⁻¹	a
Porosity at depth	ϕ_∞	0.87	vol vol ⁻¹	a
Porosity e-folding distance	γ	35	cm	b
Sediment density	ρ	2.65	g cm ⁻³	c
Temperature	T	2.77	°C	a
Salinity	S	5.05		a
Advective velocity of solids at depth	v_∞	$\frac{F_{sed}}{\rho(1-\phi_\infty)}$		—
Bioturbation coefficient at sediment-water interface	D_b	1.76	cm ² yr ⁻¹	b
Bioirrigation coefficient at sediment-water interface	α	45*10 ⁴	yr ⁻¹	b
Mixed layer depth	ζ	11	cm	b
C:N ratio of organic matter	C/N	6.625	mol mol ⁻¹	d
C:P ratio of organic matter	C/P	300	mol mol ⁻¹	b
P:Fe(OH) ₃ ^α	χ^α	0.28	mol mol ⁻¹	b
P:Fe(OH) ₃ ^β	χ^β	0.23	mol mol ⁻¹	b
P:Fe(OH) ₃ ^γ	χ^γ	0.11	mol mol ⁻¹	b
P:Fe(OH) ₃ ^{β(max)}	$\chi^{\beta(max)}$	0.28	mol mol ⁻¹	b
P:Fe(OH) ₃ ^{β(pulse)}	$\chi^{\beta(pulse)}$	0	mol mol ⁻¹	b

Sources: (a) Measured; (b) Model constrained; (c) Reed et al. (2011b); (d) Redfield (1958).

Table S.4. Boundary conditions of solids and solutes at the sediment-water interface in the model. Time dependent fluxes of OM^{α,β,γ}, Fe(OH)₃^{α,β,γ}, Mn(OH)₂^{α,β}, Mn carbonates and sedimentation rate at the sediment-water interface are shown in figure 3. For all chemical species a zero-gradient boundary condition was specified at the bottom of the model domain.

Solids	Flux at sediment water interface	Unit
F FeS	0	mol m ⁻² yr ⁻¹
F FeS ₂	0	mol m ⁻² yr ⁻¹
F S ₀	0	mol m ⁻² yr ⁻¹
F FeCO ₃	0.27	mol m ⁻² yr ⁻¹
F Vivianite	0	mol m ⁻² yr ⁻¹
F Detr. P	0.034	mol m ⁻² yr ⁻¹
F Auth. P	0.03	mol m ⁻² yr ⁻¹
Solutes	BW concentration	Unit
C O ₂	0.091	mol m ⁻³
C NO ₃ ⁻	0	mol m ⁻³
C SO ₄ ²⁻	4.05	mol m ⁻³
C Fe ²⁺	0	mol m ⁻³
C Mn ²⁺	0	mol m ⁻³
C H ₂ S	0	mol m ⁻³
C NH ₄ ⁺	0	mol m ⁻³
C HPO ₄ ²⁻	0.21	mol m ⁻³
C DIC	1.5	mol m ⁻³

Table S.5. Analyses of vivianite crystals from below the SMTZ at site NB8 with electron microprobe-EDS. Vivianite crystals were collected from 3 different depths. The average value and standard deviation for each element was calculated from 7 EDS point analyses.

Element	mol %
O	37.8 ± 3.4
Na	0.4 ± 0.2
Mg	0.8 ± 0.6
Al	6.3 ± 6.2
Si	2.6 ± 1.5
P	13.5 ± 5.4
Ca	0.3 ± 0.2
Mn	6.9 ± 2.3
Fe	31.4 ± 6.3
	mol mol⁻¹
Fe/P	3.3 ± 2.0
Fe/Mn	4.7 ± 0.8
(Fe+Mn)/P	4.1 ± 2.5
Mn/P	0.8 ± 0.5
(Fe+Mn+Mg)/P	4.3 ± 2.5

Table S.6. Reaction equations implemented in the model.

Primary redox reaction equations	
$R1 = k_{\alpha,\beta} OM^{\alpha,\beta} \left(\frac{[O_2]}{K_{m,O_2} + [O_2]} \right)$	E1
$R2 = k_{\alpha,\beta} OM^{\alpha,\beta} \left(\frac{[NO_3^-]}{K_{m,NO_3^-} + [NO_3^-]} \right) \left(\frac{K_{m,O_2}}{K_{m,O_2} + [O_2]} \right)$	E2
$R3 = k_{\alpha,\beta} OM^{\alpha,\beta} \left(\frac{[Mn(OH)_2]}{K_{m,Mn(OH)_2} + [Mn(OH)_2]} \right) \left(\frac{K_{m,NO_3^-}}{K_{m,NO_3^-} + [NO_3^-]} \right) \left(\frac{K_{m,O_2}}{K_{m,O_2} + [O_2]} \right)$	E3
$R4 = k_{\alpha,\beta} OM^{\alpha,\beta} \left(\frac{[Fe(OH)_3]}{K_{m,Fe(OH)_3} + [Fe(OH)_3]} \right) \left(\frac{K_{m,Mn(OH)_2}}{K_{m,Mn(OH)_2} + [Mn(OH)_2]} \right) \left(\frac{K_{m,NO_3^-}}{K_{m,NO_3^-} + [NO_3^-]} \right) \left(\frac{K_{m,O_2}}{K_{m,O_2} + [O_2]} \right)$	E4
$R5 = k_{\alpha,\beta} OM^{\alpha,\beta} \left(\frac{[SO_4^{2-}]}{K_{m,SO_4^{2-}} + [SO_4^{2-}]} \right) \left(\frac{K_{m,Fe(OH)_3}}{K_{m,Fe(OH)_3} + [Fe(OH)_3]} \right) \left(\frac{K_{m,Mn(OH)_2}}{K_{m,Mn(OH)_2} + [Mn(OH)_2]} \right) \left(\frac{K_{m,NO_3^-}}{K_{m,NO_3^-} + [NO_3^-]} \right) \left(\frac{K_{m,O_2}}{K_{m,O_2} + [O_2]} \right)$	E5
$R6 = k_{\alpha,\beta} OM^{\alpha,\beta} \left(\frac{K_{m,SO_4^{2-}}}{K_{m,SO_4^{2-}} + [SO_4^{2-}]} \right) \left(\frac{K_{m,Fe(OH)_3}}{K_{m,Fe(OH)_3} + [Fe(OH)_3]} \right) \left(\frac{K_{m,Mn(OH)_2}}{K_{m,Mn(OH)_2} + [Mn(OH)_2]} \right) \left(\frac{K_{m,NO_3^-}}{K_{m,NO_3^-} + [NO_3^-]} \right) \left(\frac{K_{m,O_2}}{K_{m,O_2} + [O_2]} \right)$	E6
$R7 = k_1 DIC \left(\frac{K_{m,SO_4^{2-}}}{K_{m,SO_4^{2-}} + [SO_4^{2-}]} \right) \left(\frac{K_{m,Fe(OH)_3}}{K_{m,Fe(OH)_3} + [Fe(OH)_3]} \right) \left(\frac{K_{m,Mn(OH)_2}}{K_{m,Mn(OH)_2} + [Mn(OH)_2]} \right) \left(\frac{K_{m,NO_3^-}}{K_{m,NO_3^-} + [NO_3^-]} \right) \left(\frac{K_{m,O_2}}{K_{m,O_2} + [O_2]} \right)$	E7
Secondary redox and other reaction equations	
$R8 = k_2 [O_2] [NH_4^+]$	E8
$R9 = k_3 [O_2] [Fe^{2+}]$	E9
$R10 = k_4 [O_2] [FeS]$	E10
$R11 = k_5 [O_2] [FeS_2]$	E11
$R12 = k_6 [O_2] [\sum H_2S]$	E12
$R13 = k_7 [O_2] [CH_4]$	E13
$R14 = k_8 [Fe(OH)_3^{\alpha}] [\sum H_2S]$	E14
$R15 = k_9 [Fe(OH)_3^{\beta, \beta(max), \beta(pulse)}] [\sum H_2S]$	E15
$R16 = k_{10} [Fe^{2+}] [\sum H_2S]$	E16
$R17 = k_{11} [FeS] [\sum H_2S]$	E17
$R18 = k_{12} [S^0]$	E18
$R19 = k_{13} [Fe^{2+}] [S^0]$	E19
$R20 = k_{14} [SO_4^{2-}] [CH_4]$	E20
$R21 = k_{15} [Fe(OH)_3^{\alpha, \beta, \beta(max), \beta(pulse)}] [CH_4]$	E21
$R22 = k_{16} [Fe(OH)_3^{\alpha}]$	E22
$R23 = k_{17} [Fe^{2+}] [HCO_3^-]$	E23
$R24 = k_{18} [Fe_3(HPO_4^{2-})_2] [\sum H_2S]$	E24
$R25 = k_{19} [Mn^{2+}] [HCO_3^-]$	E25
$R26 = k_{20} [Mn^{2+}] [O_2]$	E26
$R27 = k_{21} [Mn(OH)_2^{\alpha, \beta}] [HPO_4^{2-}] [Fe^{2+}]$	E27
$R28 = k_{22} [Mn(OH)_2^{\alpha}] [\sum H_2S]$	E28
$R29 = k_{23} [Mn(OH)_2^{\beta}] [\sum H_2S]$	E29
$R30 = k_{24} [Mn(OH)_2^{\alpha}]$	E30
$R31 = k_{25} [Mn(OH)_2^{\alpha, \beta}] [CH_4]$	E31
$R32 = k_{26} [Fe(OH)_3^{\beta, \beta(max), \beta(pulse)}] [HPO_4^{2-}]$	E32

Table S.7. Reaction parameters used in the model.

Parameter	Value	Unit	Source	Values in literature
k_α	0.3	yr^{-1}	a,b	0.05-1.62
k_β	0.0086	yr^{-1}	b,h	0.0025-0.0086
K_{O_2}	20	$\mu\text{m L}^{-1}$	c	1-30
$K_{NO_3^-}$	4	$\mu\text{m L}^{-1}$	c	4-80
$K_{Mn(OH)_2}$	4	$\mu\text{m g}^{-1}$	c	4-32
$K_{Fe(OH)_3}$	65	$\mu\text{m g}^{-1}$	c	65-100
$K_{SO_4^{2-}}$	1.6	$\mu\text{m L}^{-1}$	c	1.6
k1 (E7)	0.044	yr^{-1}	i	0.0011
k2 (E8)	10000	mmol yr^{-1}	c,d	5000-39000
k3 (E9)	$1.4 \cdot 10^5$	mmol yr^{-1}	c	$1.4 \cdot 10^5$
k4 (E10)	300	mmol yr^{-1}	c	300
k5 (E11)	1	mmol yr^{-1}	c	1
k6 (E12)	160	mmol yr^{-1}	c	160
k7 (E13)	10^7	mmol yr^{-1}	c	10^7
k8 (E14)	55	mmol yr^{-1}	c,g,i	8-100
k9 (E15)	44	mmol yr^{-1}	c,j	0.004-100
k10 (E16)	9000	mmol yr^{-1}	b,d	100-14800
k11 (E17)	10^{-15}	mmol yr^{-1}	e,i	0.0003-3.15
k12 (E18)	3	yr^{-1}	f	3
k13 (E19)	0.0025	mmol yr^{-1}	f,g	0.001-7
k14 (E20)	17	mmol yr^{-1}	c,g	10(c)-120(g)
k15 (E21)	0.0021	mmol yr^{-1}	g,i	$1.6 \cdot 10^{-7}$ - 0.0074
k17 (E23)	0	mmol yr^{-1}	i	0.0027
k18 (E24)	$8 \cdot 10^{-4}$	mmol yr^{-1}	i	$8 \cdot 10^{-4}$
k19 (E25)	0.265	mmol yr^{-1}		Model constrained
k20 (E26)	1200	mmol yr^{-1}	c	800-20.000
k21 (E27)	0.002	mmol yr^{-1}	f	2
k22 (E28)	0.5	mmol yr^{-1}	c	<100.000 (20)
k23 (E29)	0.4	mmol yr^{-1}	c	<100.000 (20)
k24 (E30)	1.8	yr^{-1}	f	1.8
k25 (E31)	0.0017	mmol yr^{-1}		Model constrained
k26 (E32)	3	mmol yr^{-1}		Model constrained
Vmax	10^{-6}	yr^{-1}		Model constrained
half saturation conc. Fe^{2+}	1000	$\mu\text{mol yr}^{-1}$		Model constrained
half saturation conc. HPO_4^{2-}	1000	$\mu\text{mol yr}^{-1}$		Model constrained

Sources: ^a(Moodley et al., 2005); ^b(Reed et al., 2011b); ^c(Wang and Van Cappellen, 1996); ^d(Reed et al., 2011a); ^e(Rickard and Luther, 1997); ^f(Berg et al., 2003); ^g(Rooze et al., 2016); ^h(Reed et al., 2016); ⁱ(Egger et al., 2016a); ^j(Egger et al., 2016b);

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