Interactive comment on "Variations in river input of iron impact sedimentary phosphorus burial in an oligotrophic Baltic Sea estuary" *by* Wytze K. Lenstra et al.

Anonymous Referee #1

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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.

Scientific Questions and Issues:

Title and Abstract:

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

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.

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?

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

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

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.

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

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?

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).

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?

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

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).

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.

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? 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?

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?

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.

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.

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.

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+.

Detailed comments:

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

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

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.

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

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.

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.

Fig. S.7. seems to belong with Fig. 10 (which actually cites Fig. S.7. in the caption).