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Discussion Paper



Interactive comment on "Phosphorus recycling in sediments of the Central Baltic Sea" *by* L. Viktorsson et al.

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p. 469, 18 and p. 471, 6:

We agree that the description of the sediment and pore water profiles needs to be considerably revised, and it will be in the revised version of the manuscript. The changes will be further discussed in our response to comments below on Figure 4 and on burial efficiency.

p. 471, 10:

To improve clarity, Figure 4 will show only pore water profiles of DMn, DFe and DIP and not TP profiles in the revised manuscript. TP profiles are already shown in another Figure. We will also make each panel in Figure 4 larger; the final figure should be two

column widths. It would have been interesting to see any bottom depth dependence in the Fe and Mn surface sediment pore water gradients. But we consider this data set to be too small to show any such dependencies. However, we choose to keep the Fe, Mn and DIP data in one plot to show that there is a relation between these variables. We cannot see that the paper by Dellwig et al. (GCA 74, 2010) is very relevant in this context since it deals with redox cycling in the water column, and we are discussing sediments. Dellwig et al. (GCA 74, 2010) show the vertical separation of Mn and Fe redox cycling in the water column, and that is a well-known phenomenon also in sediment. However, we did not notice much of this in the Baltic sediments we studied.

p. 471, 15-20:

It is correct that the Fe currently dissolved in the pore water at anoxic bottoms will not be the primary source of the Fe-oxyhydroxide inventory that may build up after prolonged oxygenation of the deep water, as described by Jilbert T. However, the low DFe/DIP ratio in the pore water indicates that the trapping efficiency of DIP by Fe oxyhydroxides upon oxygenation of the bottom water is very limited on shorter timescales. This information is valuable as oxygenation events at these depths in the Baltic proper are very short lived. In the revised manuscript, we will clarify that our estimate of how much of the DIP pool in the pore water that could potentially be co-precipitated by Fe during a positive redox turnover is valid only for short time scales, and that prolonged oxic conditions would result in an increase in the rate of supply of Fe oxyhydroxides to the sediment (through input from the overlying water) and a higher trapping efficiency of DIP.

p. 472, 15-25

We would like to thank Jilbert T. for clarifying our misinterpretations of the results from their paper, which was partly due to the difficulty of extracting information from very busy figures in the Jilbert et al. (2011) paper. We agree that much of our findings are similar, for example that DIP is preferentially remineralized from organic matter under

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anoxic conditions, as shown by low DIC:DIP ratios in our study and low NH4:DIP ratios in Jilbert et al. (2011) at anoxic bottoms. Regarding the DIP fluxes and their dependence on bottom depth, our data and those presented in Jilbert et al. (2011) agree fairly well when looking exclusively at data from deeper than 90 m depth – a general increase with increasing water depth. However, we maintain that there is a discrepancy between our studies when comparing the full sets of data, as the highest DIP fluxes in Jilbert et al. (2011) were found at the shallower stations (i.e., at depths 48-90 m). In contrast, we saw a general trend of much higher DIP fluxes from sediments at 124-210 m than from sediments at 30-90 m. Partly, this may be related to that all but three of the group 1 sites in Jilbert et al. (2011) were hypoxic at time of sampling whereas sediments at 30-90 m in our study was mainly oxic. However, our observation that the DIP flux is higher on anoxic bottoms than on oxic, supported by a large number of measurements, is not supported by the Jilbert et al. (2011) study. We cannot determine to what (if any) extent this may be related to methodological differences. However, we think that there is a clear indication that some of the group 1 DIP flux estimates in Jilbert et al. (2011) are overestimations, as the highest fluxes in the entire data set comes from the three stations that were oxic at the time of sampling (BY2, LF1 and LF1.5). We suspect that applying Fick's Law methodology on pore water profiles from oxic sediments may result in an overestimation of DIP effluxes to the bottom water if the vertical resolution of the pore water profile is too coarse to capture the trapping of upward diffusing DIP in the top millimeters of oxidized sediment. Another discrepancy between our study and the study by Jilbert et al. (2011) is that our fluxes on anoxic bottoms (deeper than 90 m) appear considerably higher than those deeper than 90 m in Jilbert et al. (2011). Our average DIP flux for those sites is comparable in magnitude to the maximum DIP flux in Jilbert et al. (2011) (station F80).

We realize that the discussion regarding the similarities and discrepancies between our study and the studies by Jilbert et al. (2011) and Mort et al. (2010) is incomplete and we will make necessary improvements in the revised version. We apologize for incorrectly implying that the depth range of stations in Jilbert et al. (2011) was too

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narrow. We were mainly referring to the study by Hille et al. (2005) when writing this. This unfortunate mistake will be removed in the revised manuscript.

p. 473, 1-20:

We thank the referee for clarifying that microelectrodes were used by Jilbert et al. (2011) and Mort et al. (2010) to ensure that no oxidation artifacts could have arisen during the handling of their sediment cores. Naturally, in the light of this new information, we will not include any speculation that oxygenation may have led to underestimations of DIP fluxes by Jilbert et al. (2011) and Mort et al. (2011). We agree that the full range of DIP fluxes in Jilbert et al. (2011) (0.01-0.8 mmol m-2 d-1) is rather similar to the full range in the present study. However, as the highest fluxes in Jilbert et al. (2011) ano use from "oxic- seasonally hypoxic" sediments, a direct comparison of these ranges is somewhat misleading. Thus, we maintain that our DIP flux range from anoxic bottoms between 124-210 m (\sim 0.2-0.7 mmol m-2 d-1) is generally above the range for the comparable group 2 sediments in Jilbert et al. (2011) (\sim 0-0.4 mmol m-2 d-1) and also much higher than comparable stations in especially Hille et al. (2005), but also in Mort et al. (2010). We will revise the discussion and be more precise in our comparisons.

We are currently working on a comparative analysis of ex situ and in situ approaches to estimate benthic fluxes from anoxic sediments. Preliminary data indicate that such estimates agree rather well. We will rewrite the discussion on p. 473, L. 1-20 and emphasize that special attention needs to be taken when evaluating ex situ measured fluxes where oxidation artifacts cannot be excluded, rather than excluding the method as a whole.

p. 475, 20-30

Our data set shows, that both the magnitude of the DIP fluxes and the DIC:DIP flux ratios are higher and lower, respectively, at anoxic bottoms compared to oxic. Looking at anoxic data separately the DIC:DIP flux ratio is not observed to decrease with in-

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creasing water depth, and no significant depth dependent trend of this ratio is evident at the anoxic sites of our study.

Regarding the advantages/disadvantages between using NH4 or DIC as a measure of the organic matter degradation rate we find DIC to be superior to NH4, especially along a transect from oxic to anoxic bottoms (e.g. Andersson et al., 1986). The main disadvantages of using NH4 are that NH4 can be nitrified to NO3 at oxic sites and thereafter be converted to N2 through anammox or denitrification below the oxygenated surface layer of the sediment. The NH4 or NH4 + NO3 flux will therefore underestimate the organic carbon oxidation rate. Also, as the C/N ratio in fluxes from anoxic sediments generally is higher than Redfield stoichiometry, using NH4 as a measure may underestimate carbon oxidation rates. The contribution to DIC from methane oxidation is negligible in this environment, because the methane concentrations are about 4 orders of magnitude smaller than the DIC concentrations in bottom water and surface sediment (Baltic Gas project, pers. comm.). Methane is most likely oxidized (anoxically) in these sediments, but it will not be noticeable on the DIC concentration.

Sections 4.4 and 4.5 – Burial

The focus of our measurements was the DIP fluxes between sediment and water, therefore limited resources could be spent on detailed P sediment studies and P burial. Of course our results would have been more conclusive if we would have had resources to also measure P fractions in sediment and sediment accumulation rates. However, this was not the main focus in our study and we find that the principal message of the manuscript is the DIP flux measurements and not the P burial.

We further evaluated P burial efficiency as encouraged by Jilbert T. There are two variables measured that can be used for this, the P content in the sediment and the sediment accumulation rate. Of these two variables the sediment accumulation rate is far more spatially variable than the sediment P content (on anoxic bottoms alone). This means that the calculation of the burial efficiency will be far more reliable based

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on the sediment accumulation data than on the P content data, since the variability of SAR will determine the variability of burial rates to larger extent than sediment P content. This was the main reason that we used sediment accumulation data from Hille et al. (2006), because they have an impressive number of sampling points, 52 cores. In an up-dated manuscript we will instead give a range of P burial and thus a range of P-burial efficiency. The lower range of the TP burial is given by the lowest sediment accumulation measured by Hille et al. (2006) (10.5 g m-2 yr-1) and the TP concentration at 10 cm depths at station E and F (30 μ mol g-1) and the higher range given by the highest sediment accumulation measured by Hille et al. (2006) (527 g m-2 yr-1) and the TP concentration at 2 cm depths at station E and F (ca 35 μ mol g-1, as suggested by Jilbert T.). This gives a TP burial range of 0.001-0.051 mmol m-2 d-1 and a range of burial efficiency of 0.2-12%.

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