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Interactive comment on "Beyond the Fe-P-redox connection: preferential regeneration of phosphorus from organic matter as a key control on Baltic Sea nutrient cycles" *by* T. Jilbert et al.

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Title: Beyond the Fe-P-redox connection: Preferential regeneration of phosphorus from organic matter as a key control on Baltic Sea nutrient cycles Author(s): T. Jilbert et al.

I was delighted to see that serious scientific effort is being invested in clarifying natural causes for "eutrophication" of the Baltic Sea, because the managerial mainstream (for example: http://www.helcom.fi/BSAP_assessment/eutro/HEAT/en_GB/status/) apparently chooses to ignore the natural anoxia-productivity-feedback that the present paper is examining. I am also pleased that our at that time controversial concept of "natural eutrophication" via the Fe-P connection (Emeis et al., 2000; the original publication

on this process was that by Einsele, 1936; see below) has made it into the scientific mainstream, although I feel that it is being somewhat undersold in the present paper in comparison to subsequent publications. But that feeling was shared by Prof. E. Emelyanov when I first told him of our great new discoveries about the Baltic Sea in the early 1990′s and all he said was "Well, we published that 20 years ago already!" And then, more silently: "But in Russian. . .". In the same vein: Please excuse me for pointing out references that you may or not know, find interesting or relevant, but which bear on the subject matter (and also push the IOW boat occasionally).

So, although the phenomena described are not new (I believe the original paper is by Einsele, W., 1936. Über die Beziehungen des Eisenkreislaufs zum Phosphorkreislauf im eutrophen See. Arch. Hydrobiol., 29: 664-686 instead of Mortimer), and the role of preferential regeneration of P may be unsurprising (see below), this is a solid piece of work that is well written, well structured (but somewhat too long for my taste, see below) and well illustrated. It will certainly become a well cited piece of evidence that occasionally processes other than human impacts alter conditions in marine environments. There are some aspects that I ask the authors to consider in a revision, which I advocate before the paper is accepted.

First: In the introduction, there is a general claim that the Baltic Sea is generally eutrophied and that the area of anoxic seafloors has increased over the last 100 years. The references given (Conley et al., 2009 a or b? Fonselius, 1981 and Savchuk et al., 2008) are unsuited to substantiate that claim, because no original data on sediment facies are given there. One of the few empirical publications on this (as far as I know) is Jonsson, P., Carman, R. and Wulff, F., 1990. Laminated sediments in the Baltic - A tool for evaluating nutrient mass balances. Ambio, 19(3): 152 - 158. Later in the manuscript, the extent of seafloor covered by anoxic waters is discussed, which is largely controlled by the frequency (and possibly the season) of salt water inflows (Zorita, E. and Laine, A., 2000. Dependence of salinity and oxygen concentrations in the Baltic Sea on large-scale atmospheric circulation. Climate Research, 14: 25-41.

This paper is interesting because it clearly shows that eutrophication by human action does not play a significasnt role, and that instead regional/hemispheric climate dictates the environmental condition in the Baltic Proper. By the way, similar conditions as today have prevailed there (in the central Baltic Sea) since the mid-Holocene, with ample evidence of cyanobacterial blooms (Bianchi, T.S., Engelhaupt, E., Westman, P., Andrén, T., Rolff, C. and Elmgren, R., 2000. Cyanobacterial blooms in the Baltic Sea: Natural or human-induced? Limnol. Oceanogr., 45(3): 716-726) and higher productivity than today (Emeis, K.-C., Struck, U., Blanz, T., Kohly, A. and Voß, M., 2003. Salinity changes in the Central Baltic Sea (NW Europe) over the last 10000 years. The Holocene, 13(3): 413-423). Makes sense, too, because there was much more salty deep-water at that time. . ..

The paper makes a point of attributing differences in pore water profiles to P regeneration from OM versus desorption by FeOOH; this distinction is made throughout the text, but is in my opinion misleading. The basic process is mineralisation of phosphate from organic matter, everywhere and under all conditions. If conditions at the sediment-water interface permit presence of oxidized iron hydroxides, the diffusion of P into the bottom water is hindered by adsorption onto these surfaces. When iron is reduced, PO4 is liberated. This is nicely illustrated in the deep-water (>150 m) phosphate and oxygen concentrations given in Emeis et al. (2000): Until approximately 1983, oxygen fluctuated around 0 mL/L and phosphate concentrations in deep water varied significantly (because the iron-bound phosphate pool was sporadically liberated). After appr. 1983, there was a long (until 1993) trend of increasing PO4-concentrations in (anoxic) deep water, which was fed by unhindered diffusion of phosphate out of the sediments. This long-term increase in deep-water phosphate concentrations is probably independent of the area covered by anoxic waters (an increase in area increases the volume of water to be charged with phosphate, but I don′t know for certain – has that been modelled?), but rather is dependent on the concentration gradient of phosphate in the pore waters of sediments under the anoxic lid. As soon as oxygen hits the anoxic and Fe-rich waters, though, all phosphate is re-scavenged – and is probably transported

into the deep basins (see below) in the particulate phase near bottom.

Interestingly, in the pore water profiles of the present paper and the data set in Hille et al., (2005) there is no evidence for the supposed final P-sink (apatite formation) deeper in the sediment, but instead PO4 concentrations continue to increase to total core depth. I remember that trace element and majoir element statistics suggest a strong association of P with newly formed Ca,Mg-carbonates, but don′t remember where I saw that. Thus I wonder if the supposed near-bottom regeneration of "fresh" organic matter alone feeds the phosphate efflux, or if instead the entire drawn-out porewater gradient is the supply. As pointed out below, seasonal supply of "fresh" OM is questionable in the first place, because lateral transport dominates everywhere.

There is a twist to this which concerns the relationship between anoxic area and amount of phosphate liberated, and the observed higher C:P ratio in deeper waters. Material budgets of the central Baltic Sea (and all other accumulation areas in the entire Baltic) are strongly dominated by lateral transport, as seen in invariably much higher sediment trapped in deep than in shallow traps in the Gotland basin. Conditions in shallow-water areas on the other hand are conducive to adsorption of phosphate onto FeOOH, which is then transported (along with organic matter, trace metals, pollutants and generally, fines) into the deep parts of the sedimentation basins (Laima, M.J.C., Matthiesen, H., Christiansen, C., Lund-Hansen, L.C. and Emeis, K.-C., 2001. Transport of P, Fe and Mn along a depth gradient in the SW Baltic. Boreal Environmental Research, 6: 317-333; Emeis, K.-C., Christiansen, C., Edelvang, K., Jähmlich, S., Kozuch, J., Laima, M., Leipe, T., Löffler, A., Lund-Hansen, L.L., Miltner, A., Pazdro, K., Pempkowiak, J., Shimmield, G.B., Shimmield, T., Smith, J., Voß, M. and Witt, G., 2002. Material transport from the near shore to the basinal environment in the Southern Baltic Sea, II: Origin and properties of material. Journal of Marine Systems, 35(3-4): 151-168.). That means, we have a concentration mechanism for phosphate in those parts of the basin, where presence of dense water increases the incidence of anoxic conditions (see Zorita and Laine reference above). In my opinion, the coincidence of physical transport and sorting creates different initial C:P ratios in the deeper basins.

In the paper, parts of the Discussion deal with influences of external factors (climate, stagnation expansion/contraction) on the DIP cycle, and look at the specific situation of the Farö Deep for support. In my opinion, the paragraphs 3.3. and 3.4. could be shortened. I wonder, for example, what effect on the burial of P an expansion of the anoxia zone may have, because the upper depth limit of sedimentation in the central Baltic Sea is determined by internal waves in the pycnocline – no sediments are deposited in the vicinity of the pycocline because they are immediately resuspended and end up in the mud accumulation areas below. The Farö Deep situation clearly differs from the deeper Baltic Central, because it is ventilated much more frequently by winter water formation, if I am not mistaken.

In summary, the paper is essentially publishable as it is, but would benefit from a more critical evaluation of alternative ideas. My suggestions above are not comprehensive, I am sure, but are not meant as substantial criticism of the data, concepts, and interpretations of the paper, which is a data-rich and excellently written revisit of what has already been published based on much less data. The manuscript is not as concise as it could be, and I have the feeling that in several instances the authors make more of their own (and other people′s)observations than these deserve. Maybe this can be improved in a revision.

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