Biogeosciences Discuss., 8, C582–C591, 2011
www.biogeosciences-discuss.net/8/C582/2011/

Biogeosciences Discussions

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.

T. Jilbert et al.

t.jilbert@geo.uu.nl

Received and published: 15 April 2011

REVIEWER: 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).

AUTHORS: We must admit to being unaware of the early Russian literature on this topic. On the other hand we fully acknowledge the contribution of Kay Emeis and his colleagues to the study of the phosphorus cycle of the Baltic; indeed the Emeis et al. (2000) paper was referenced several times in the original version of our manuscript. Furthermore, and this is an important point, we would like to emphasise that our paper is focused on the influence of preferential remineralization of P during organic matter decay, rather than the interaction between Fe-oxides and P, on fluxes within the P cycle on the basin-scale. This is a crucial distinction; it allows us to take a step forward from existing knowledge because no previous study has attempted to demonstrate and quantify the importance of this process in the Baltic Sea.

REVIEWER: 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.

AUTHORS: We have now included the Einsele reference alongside that of Mortimer.

REVIEWER: 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. C168).

AUTHORS: We have altered the references for the statement concerning the expansion and exacerbation of hypoxia during the 20th century. We replace Fonselius (1981) with Fonselius and Valderrama (2003) as the latter publication specifically investigates the changes in water column oxygen concentrations (ie. the most direct measure of the severity of hypoxia) over the last century. The Conley et al. reference is "2009a" and this is now given, and the Jonsson et al. (1990) reference is also included as suggested. We believe that all three references are suitable to back up the claim of enhanced severity and spatial extent of hypoxia through the course of the 20th century; the direct water column oxygen data reported in Conley et al. (2009a) and Fonselius and Valderrama (2003) are fully complimentary to the distribution of laminated sediments reported by Jonsson et al. (1990). Furthermore, we decided to retain the Savchuk et al. (2008) reference, as this study shows by means of biogeochemical modeling that enhanced anthropogenic nutrient loading during the 20th century very likely drove the system towards the current hypoxic state.

REVIEWER: 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. . ..

AUTHORS: We agree that "regional/hemispheric climate dictates the environmental condition in the Baltic Proper" on the multidecadal timescale in the late 20th century; specifically, climate dictates the inflow-stagnation cycle and this has a large influence on the oxygen and nutrient cycles. However we also believe that, as shown by Savchuk et al. (2008), the system has been forced into a eutrophied state which is now maintained by the geochemical feedbacks we describe. In response to the statement about paleoceanographic conditions in the Baltic, we are aware that hypoxia/anoxia existed during the pre-anthropogenic era and have included this as the new opening statement of the introduction. However as shown by the laminated sediment records in Zillen et al. (2008) such conditions were intermittent, and the 20th century hypoxia is indeed severe with respect to the immediately preceding centuries (see also Jonsson et al., 1990).

REVIEWER: 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 sedimentwater 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, PO_4 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.

AUTHORS: One advantage of our approach – ie. the generation of porewater profiles of multiple dissolved constituents – is that the various diagenetic processes affecting phosphorus can be observed independently. We acknowledge that porewater phosphate is initially derived from organic matter decay and have added lines to clarify this in the text (Introduction and Section 3.1). However, the dynamic subsequent interaction with Fe-oxides is responsible for large variability in porewater profiles and effluxes of P. We do not believe it is misleading to distinguish between instantaneous porewater phosphate contributions from these two sources. Rather, we can use ammonium profiles to predict the shape and range of the phosphate profiles based on organic matter decay alone, identify deviations from these and use the porewater iron data to confirm whether the deviations are related to Fe-oxide dissolution (as is done in Figure 3). This approach provides a far more complete picture of the geochemical processes responsible for P regeneration than studying water column concentrations alone.

AUTHORS: The 1970-2000 sequence of events in the Gotland Basin described in Emeis et al. (2000) and summarized above is entirely complimentary with our interpre-

tations. We agree that the long-term increase in deep-water phosphate concentrations from the early 1970s to the early 1990s is mainly derived by the unhindered efflux of P from anoxic sediments, and that the shrinking total hypoxic/anoxic area of this interval would not in itself influence the concentration of P in the deep water. However it is important to distinguish between deep-water P concentrations such as those shown Fig. 7 of Emeis et al. (2000) and the total DIP pool of the Baltic (eg. as discussed in Conley et al., 2002). At a deep monitoring station like the Gotland Deep, the deep-water P concentration could theoretically continue to increase during this interval, even while the whole basin DIP pool became depleted due to drawdown into Fe-oxides along the basin margins. In fact, what we show is that the release of P from the sediments in the deep basin was so great (due partly to preferential remineralization) that it outweighed the drawdown into Fe-oxides and led to a net increase in the total DIP pool from the early 1970s to the early 1990s (Fig. 6a).

REVIEWER: 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.

AUTHORS: As shown with detailed analyses of sediment and porewater geochemistry by Mort et al. (2010), apatite formation does not appear to be important in near-surface sediments throughout much of the Baltic. Both our porewater phosphate profiles and those of Hille et al. (2005) also support this interpretation in that phosphate continues to increase to the lower boundary of the multicores used in these studies. Only in the Landsort Deep did Mort et al. (2010) find evidence for intermittent apatite formation in recent sediments. There, sedimentary apatite peaks do indeed coincide with peaks in Mn-Ca carbonates, suggesting that the formation processes may be related. Further discussion of this issue lies outside the scope of this paper, however.

AUTHORS: In terms of the source of phosphate for the flux across the sediment-water interface, it can be seen in Figure 2 that the phosphate profiles (except where influenced by Fe-oxide dissolution) are generally asymptotic in shape, implying that the surface sediment is indeed the location of active dissolved phosphate generation (as summarized in Section 3.1 of Schulz and Zabel, "Marine Geochemistry"). Our work on reactive transport modeling of diagenesis in Baltic Sea sediments confirms that this is the case (Reed et al., L&O in press).

REVIEWER: 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.

AUTHORS: We are aware that lateral transport of sedimentary material towards the deep basins is extremely important in the Baltic. There are several ways in which this process could influence our observations of the P cycle, which are not fully distinguished in the above comment. In each case we have adjusted the manuscript to acknowledge the potential impact on our data and interpretations (see details below):

1. Transport of P associated with Fe-oxides may lead to concentration of dissolved P in the deep-basin water column, due to dissolution of these oxides upon entry into the reducing zone. This accumulation of dissolved phosphate in the deep waters could potentially influence the budget calculations of Gustafsson and Stigebrandt (2007), and the DIP values reported in Conley et al. (2002) which we discuss in Section 3.3. We show with our budget (Table 1) that preferential remineralization can account for most, but not all, of the 'additional' P required to balance the budget of Gustafsson and Stigebrandt (2007) for fully anoxic stagnations. We now acknowledge in Section 3.3 that dissolution of laterally-transported Fe-P likely accounts for the remaining amount, and that it could play a role in the increase in the total DIP pool over the early 1970s to early 1990s. The reference of Emeis et al. (2002) is also included.

2. Lateral transport of organic matter may lead to higher concentrations of older, more degraded organic matter in the deep basins. This material potentially has different C:P and N:P ratios from the organic matter which arrives vertically from recent export production, and thus could affect the sedimentary Corg:Porg data we plot in Figure 4. The change in C:P and N:P ratios during degradation will depend on the prevailing oxygen conditions, which of course will vary during transport of the material downslope into the deep basin. Estimating the transport path of material accumulated at a specific deep basin location is clearly very difficult, but in general terms a contribution from older, degraded material at the deepest sites would be expected to shift the net C:P and N:P towards lower values with respect to newly-exported material, because the latter

has been subjected to immediate anaerobic (hence C- and N- enriching) degradation, while the former has probably spent at least some time degrading in the oxic zone. This is suggested by the data points for sites 16 and 17 in Figure 4, which plot to the left of the predicted increase in sedimentary C:P and N:P with water-depth. We have adjusted the text of Section 3.2 to make this point more clear.

3. The accumulation of old, degraded organic matter in the deep basins could potentially influence the fluxes of NH4 and PO4 across the sediment-water interface, if ongoing breakdown of this material occurred, hence affecting the flux ratio data in Figure 4. However, it can be seen that the two stations with apparently the strongest influence of laterally-transported organic matter (16 and 17, see previous point) show no deviation in their NH4 / PO4 flux ratio from the trend of the other sites. This observation suggests that the laterally transported material at these sites is relatively refractory, and is not actively degrading further in a way which impacts upon the fluxes of NH4 and PO4. We have adjusted the text of Section 3.2 to make this point more clear.

REVIEWER: 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.

AUTHORS: Section 3.3 has been shortened as requested by both reviewers. We cannot comment in general on the influence of pycnocline waves on phosphorus burial, except to say that the sites we studied display evidence of continuous deposition of sediment throughout the last century (based on the lack of hiatus in the 210Pb pro-

files). The Fårö Deep is in fact very similar to the central (Gotland) Basin in terms of the ventilation history and this is shown by the good correlation between the oxygen concentration in Fårö Deep and the basinwide total hypoxic area (Figure 7).

REVIEWER: 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.

AUTHORS: We have tried to address and evaluate the alternative interpretations raised in this review, and to make the manuscript more concise where suggested. We also wish to highlight again that the qualitative and quantitative assessment of the role of enhanced regeneration of P from organic matter for Baltic Sea nutrient cycling has not been addressed in earlier work and thus is novel. We thank the reviewer for the positive general comments, and we hope that our modifications have satisfied his concerns.

Interactive comment on Biogeosciences Discuss., 8, 655, 2011.