

Interactive comment on “Modeling benthic-pelagic nutrient exchange processes and porewater distributions in a seasonally-hypoxic sediment: evidence for massive phosphate release by *Beggiatoa*?” by A. W. Dale et al.

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First and foremost, we would like to take this opportunity to express our gratitude to the referees for their time in reviewing our manuscript and the constructive nature of their comments. We have tried to address their points as far as possible and in doing so the manuscript is, in our opinion, much improved.

To begin with, both referees agree on the following points:

1) The paper is long

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2) There is a lack of data on solid phases and on abundance and distribution on *Beggiatoa* as well as their ability to store nitrate and phosphate at the site investigated

Regards the first of these, we have shortened the methodology section by moving the description of the bioirrigation experiments to the Supplementary Material. It was necessary to keep some detail here, particular the reference to the two bioirrigation parameters that are determined from the experiments and subsequently imposed in the model.

The second point is clearly a good one, and we acknowledge that the strength of our conclusions is weakened by a lack of solid phase data and the intracellular P content. The field campaign was not designed to assess the fate of iron and phosphorus in the sediment, and the striking phosphate dynamics was a fortuitous observation made very late in the sampling programme. Unfortunately, nothing can be done about this now, but this is something that we want to address in future. Of more relevance to this study is the capacity of the strain of *Beggiatoa* at Boknis Eck to store nitrate and phosphate. The abundance and distribution of these bacteria as well as their nitrate-storing capabilities has been documented previously (Preisler et al., 2007). Marine *Beggiatoa* are also known to take up and store P (Goldhammer et al., 2010; Brock and Schulz-Vogt, 2010), yet we do not know anything about the ability of the *Beggiatoa* at Boknis Eck to store phosphate. At the same time though, the rates of bacterial P uptake and release are on the same order as those previously reported for predicted by giant sulfide oxidizing bacteria (Goldhammer et al., 2010; Schulz and Schulz, 2005). Our model results raise new hypotheses concerning P cycling in Boknis Eck sediments and the possibility that bacterially-mediated P cycling is common at sites with bottom waters that oscillate between oxic-hypoxic and/or anoxic conditions. Whilst we agree that this is speculative without the necessary time-series data on the P content of *Beggiatoa*, we hope that this will inspire further investigations into the ecology of these bacteria at this and similar sites. We have been quite frank about the uncertainties of the model results in the conclusions and abstract and it is not our intention to present this result as hard

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evidence (hence also the interrogative in the manuscript title). We have nonetheless echoed the referees' comments in the conclusions that the mechanism and regulation of P storage in bacteria is poorly understood and that it is not known whether the strain of bacteria at Boknis Eck is capable of intermediate polyphosphate storage.

Referee #1 goes on to make three further interesting commentaries:

- 1) There may be a smearing of concentrations by the application of rhizons
- 2) The model ignores potential oxygen debts and excesses extending into following years
- 3) Time series bottom water nutrient data are not included in the model

Regarding the use of rhizons, we have a lot of experience with their application and also their limitations. We only sampled enough porewater to cover the chemical analyses which was on the order of 5 ml. Sampling this volume at 1 cm intervals with rhizons should not lead to significant artifacts. Comparison of the rhizon data with the squeezed samples revealed no obvious bias in the rhizon data due to smearing, both at Boknis Eck and many other locations where we have applied both techniques simultaneously. Of more importance, in our opinion, is the spatial heterogeneity in porewater concentrations associated with sub-sampling the sediments from two different multiple-cores, even though both cores were retrieved with the same multiple-coring device.

The question of potential oxygen debts and excesses due to inter-annual variations in productivity, bioirrigation, length of hypoxic period etc is a valid comment, yet again one which we cannot address with data from 12 months only. This is a topic which we are currently investigating using data from a long-term monitoring programme carried out at this site since 1957 including bottom water oxygen, temperature and primary productivity. The effects of the long-term trends in these environmental forcings will be addressed in a separate manuscript. Model uncertainty associated with varying oxygen debts was mentioned in section 2.4.3.

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Following the third comment, we now show the phosphate concentrations and also the atomic N/P ratios of dissolved inorganic nutrients in the bottom water (new Fig. 7b, see below). There is, as the referee supposed, a good correlation with the flux of phosphate from the sediment and the bottom water phosphate concentration which nicely supports our calculated sediment fluxes. For the other nutrients the trends were not so clear. The elevated phosphate fluxes during hypoxia also led to a strong decrease in the atomic N/P ratio of the bottom water. Not accounting for the increase in bottom water phosphate concentration in the model will add an error to the calculated fluxes that is certainly much smaller than the uncertainty in other model parameters such as the P:Fe ratio (see below).

Referee #2 makes two remarks related to P geochemistry:

- 1) A constant P:Fe ratio of 0.1 may be unrealistic to simulate the sharp phosphate peaks
- 2) Apatite formation is not included in the model

In the spirit of Occam, we employed a constant P:Fe ratio in the model to keep the parameterizations as simple as possible without comprising realism. By using a depth-variable ratio without supporting data we would run the risk of overfitting the model, resulting in results that would be biased toward this parameterization. This is not to say that the true P:Fe ratio is bigger or smaller than 0.1, or that this ratio is constant with depth. We do not have data on the iron-bound P pool at Boknis Eck, but previous model simulations that have used a constant value supported by experimental data provided a close correspondence to field data (Slomp et al., 1996 JMR; Reed et al., 2011 L&O). Furthermore, the value used by Reed et al. (2011) for the fine-grained sediments of Arkona Basin (S. Baltic Sea) that also experiences seasonal hypoxia is similar to ours (0.175). We preferred to base our P:Fe ratio on these studies rather than on laboratory studies that may not accurately reflect the true nature of iron oxyhydroxide particles in nature (e.g. Gunnars et al., 2002). Clearly, though, a constant value of 0.1 for

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both the P:Fe ratio of the deposited iron oxyhydroxides as well as the authigenic iron oxyhydroxides precipitated at the sediment surface is subject to uncertainty. Yet, as we noted in the manuscript, the integrated phosphate concentration contained within the November peak is 2.5 times higher than the ferrous iron peak, implying that $P:Fe \approx 2.5$ (!), and we were not able to provide better solutions to the sharp phosphate peaks using $P:Fe$ ratios > 0.1 . Thus, we are reasonably confident that release of iron-bound P is not responsible for the sharp phosphate peaks that appear during hypoxia.

For the second comment, the referee asks why authigenic apatite formation was not considered. The presence of uniformly dispersed authigenic carbonate fluorapatite (CFA) is probably widespread in continental margin sediments (Ruttenburg, 2003) and apatite precipitation will be favoured by high dissolved phosphate concentrations. Given that bioirrigation and bubble irrigation conspire to maintain low phosphate concentrations in the surface sediments for much of the year, apatite precipitation is likely to be low at Boknis Eck. Moreover, Reed et al. (2011) concluded that apatite precipitation was unimportant in Arkona Basin sediments and that the sedimentary authigenic P is mainly deposited from the water column. We have added this clarification to the text. The consideration of apatite in our model would not affect our conclusions. Instead, it would lead to a faster drawdown of dissolved phosphate following the big phosphate release event in October/November. In fact, the higher predicted than measured phosphate concentrations in December may well be evidence of apatite formation.

The minor comments of referee #2 have all been addressed, including the removal of Fig. 8.

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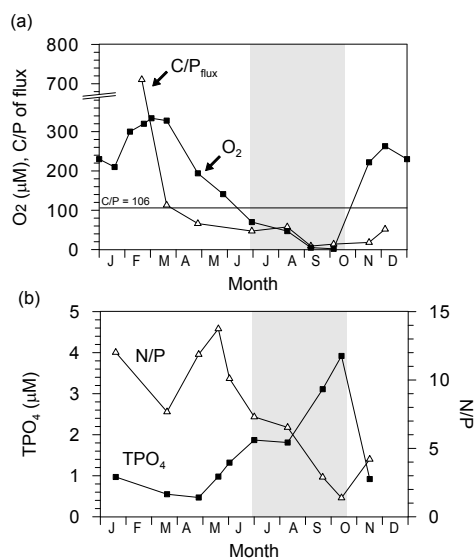


Fig. 7. (a) Oxygen concentrations (from Fig. 2c) and the stoichiometry of the TCO_2 to TPO_4 flux (C/P) by molecular diffusion at the sediment-water interface calculated using the measured data. The horizontal black line is the Redfield C/P ratio. Note the axis break in the ordinate. (b) TPO_4 concentrations and dissolved inorganic nitrogen to phosphorus atomic ratios (N/P) in the bottom water over the study period (data from Bange et al., 2011).

Fig. 1.

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