

## ***Interactive comment on “Parameterization of biogeochemical sediment–water fluxes using in-situ measurements and a steady-state diagenetic model” by A. Laurent et al.***

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In this study, the authors use a 1-D (vertical) diagenetic model to derive a series of meta-models for predicting fluxes of O<sub>2</sub>, NO<sub>3</sub> and NH<sub>4</sub> from sediments on the Louisiana shelf. The 1-D model is parameterized using an interesting genetic algorithm to continuously optimize a series of sets of parameters for a defined number of iterations (or generations). Following each iteration, a cost function is calculated based on the goodness-of-fit of the model with regards to measured benthic fluxes of O<sub>2</sub>, NO<sub>3</sub> and NH<sub>4</sub> and measured porewater NH<sub>4</sub> concentrations at two stations and at three discrete time intervals. The overall best performing model is then used in the meta-

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modelling step, which is a multivariate regression of observed fluxes against modelled fluxes derived by forcing the steady state diagenetic model with 100000 random boundary condition combinations (O<sub>2</sub>, NO<sub>3</sub> and NH<sub>4</sub> concentrations, salinity, temperature, POM flux) taken from a previous pelagic (ROMS) model study. The meta-models are then applied to simulate fluxes across the Louisiana shelf using data from the pelagic model during a discrete time period (July 2009) as a forcing.

This is an interesting study that focuses on coupling benthic processes in biogeochemical circulation models of the water column. I like the optimization approach and can see how it would be useful in my own work. I agree completely with the authors that smart ways are needed to parameterize benthic process in a computationally efficient manner, and this is a topic close to my own heart. I have some questions and comments that the authors should attend to, but there are no major flaws as far as I can see. This is a sound paper that meets the scope of the journal and I recommend publication. I hope that my comments are fair and that they will add some value to the paper (Andy Dale; adale@geomar.de)

1) The only major critique I would like to raise, and would like the authors to respond carefully to, is that the steady state meta models are applied to a highly dynamic environment with huge intra-annual variability in POM flux and bottom water O<sub>2</sub> (Fig. S1). The benthic functions are not dynamic i.e. they do not account for the storage of POM and the decoupling of solute fluxes from POM fluxes. POM deposited on the seafloor will degrade over a wide range of time scales, rather than instantaneously as the present functions assume. This approach would be permissible in a setting exhibiting less temporal variability, but not here. The authors are aware of the potential error incurred (cited Soetaert et al., 2000) but this aspect is barely discussed. I would expect quite large time lags between POM flux to the sediment and the response of the benthos to communicate the fluxes back to the water column. For instance, the NH<sub>4</sub> flux responds almost instantaneously with POM flux in their model, but since OM does not degrade instantaneously, the NH<sub>4</sub> flux in reality would lag behind POM flux and

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be more attenuated and without the pronounced flux spikes. It would really enhance the appeal of this paper if these ideas were incorporated into a couple of discussion paragraphs, with an estimate of the error in not accounting for the temporal. This result of this exercise would be a great value to both the pelagic and benthic modelling community alike, me included.

2) On similar level, on p7553 line 16+ the authors claim that using a time-varying forcing for the optimization would not have changed the results significantly given the constraint of the dataset on the optimization. This is a firm statement based on belief rather than fact. I do not agree with the authors, given the previous comments, and would prefer it if they would be more open about the possibility that a transient optimization routine, combined with a dynamic sediment component, would improve their model.

3) The POM fluxes (actually PON fluxes) in Table 1 used in the diagenetic model are taken from the pelagic model (Fig. S1). However, the tabulated fluxes in June and September for St. Z02 are up to a factor of 5 lower than in the pelagic model. Could this explain why the meta-model predictions are improved in June when the POM flux is used as an additional parameter to optimize (p7549,L10, Fig. 3)? In fact, there are other indications that the POM flux is too low. The optimized model underestimates NH<sub>4</sub> and NO<sub>3</sub> fluxes in June at Z02 (Fig. 2). Also, it requires minimal infaunal mixing, no burial of reduced compounds, and an increased T dependence on mineralization (p7548,L15+). This suggests to me that the optimized model is trying to mineralize as much POM as possible in order to fit the NH<sub>4</sub> concentrations and fluxes.

4) The optimization procedure works by firstly selecting  $n$  sets of parameters whose values are determined by adding random noise to the original parameterization of Soetaert et al. (1996). The next  $n$  sets of parameters in the following generation are based upon the best half ( $n/2$ ) parameter sets from the previous generation using the cost function, and so on, for 200 generations. The evolutionary trajectory leading to the final 'fittest' optimized set may depend more on the best fit parameterization in

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the early generations rather than the later ones. In other words, small differences in the parameterization at the start could lead to large differences at the end, resulting in a different set of optimized parameters that explain the observations equally well, analogous to following a tree trunk upwards and coming out at a different twig every time. Have the authors run through the whole procedure repeatedly to double check that the same final parameter set is predicted each time?

5) POC fluxes in this system are high ( $>100$  mmol/m<sup>2</sup>/d in summer) at station Z02, in combination with severe hypoxia (Fig. S2). I would expect high sediment porewater sulfide concentrations under these conditions and the development of sulphur oxidizing bacteria communities on the sediment surface that carry out DNRA ( $\text{NO}_3 + \text{H}_2\text{S} \rightarrow \text{NH}_4 + \text{SO}_4$ ). Can the authors justify why this process was omitted in their approach? It is not enough to reply that this process was not included in the original Soetaert model (which, incidentally, is a deep-sea application). Perhaps DNRA explains why the model does not simulate the high  $\text{NH}_4$  porewater concentrations in September at Z02 when DNRA rates would be expected to be highest. I would speculate that during the summer period, DNRA would become an important contributor to the N cycle, as observed in seasonally hypoxic settings elsewhere (Dale et al., 2013, Biogeosciences, 10, 629-651, doi:10.5194/bg-10-629-2013). Enhanced  $\text{NO}_3$  uptake by bacteria may also explain why the diagenetic and meta-models are unable to simulate high  $\text{NO}_3$  fluxes (Fig. 2 and Fig. 5c).

6) Similarly, given the severe depletion of  $\text{O}_2$  in late summer, one could expect infaunal mixing by bioturbation and bioirrigation to be dependent on  $\text{O}_2$ , in line with other observations and models (Dale et al., 2013). Please comment.

7) The rate of organic matter mineralization is temperature dependent, but other microbially mediated reactions are not. Please explain.

8) The meta model predicts a high  $\text{O}_2$  flux at zero  $\text{O}_2$  bottom water concentrations (Fig. 9a). This is strange and must be clarified.

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9) Can the authors explain why the NO<sub>3</sub> flux does not depend at all on POM flux (Table 4). After all, no POM = no diagenesis.

#### Other comments

I would personally like to see, for the sake of correctness, charges assigned to the anions, (e.g. NH<sub>4</sub><sup>+</sup> instead of NH<sub>4</sub>). But that's just my own preference.

General: font size on the figures is really, really small. Please correct this.

Table 1 and section 2.1. Please provide the water depth of the two stations.

Table 1 header. I believe that the fluxes and NH<sub>4</sub> profiles are used to optimize the diagenetic model via Eq. 3, not the boundary conditions listed in this table.

Table 4 header: Unclear 'the direction of its effect'.

P7538,L13. ...O<sub>2</sub>, NO<sub>3</sub> and NH<sub>4</sub> fluxes

P7539,L19 nitrate/nitrite

P7539,L28. Please add reference Bohlen et al. 2012 after Fennel et al., 2009. (Bohlen, L., Dale, A. W., Wallmann, K. (2012) Simple transfer functions for calculating benthic fixed nitrogen losses and C:N:P regeneration ratios in global biogeochemical models. *Global Biogeochemical Cycles* 26, GB3029, doi:10.1029/2011GB004198)

P7540,L9. Vertically integrated and depth resolved models are not the same thing. The context of this paragraph makes me believe that the authors are referring to the latter type only. Vertically integrated (to my mind) would be a sediment-transfer function or a single layer model (see Soetaert et al., 2000).

P7540,L40. ...O<sub>2</sub>, NO<sub>3</sub> and NH<sub>4</sub> fluxes

P7541. Section 2.1. Please provide some more information on how the fluxes were determined (e.g. ex situ versus in situ, no. replicates etc). The authors report a standard deviation on the measured data, which only makes sense if a reasonable

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large number of observations were made.

P7541,L17. Suggest change 'observations' to 'data'

P7541,L19. Suggest delete 'process leg'

P7541,L21+24. Suggest delete or clarify 'near shelf survey stations X'. This may mean something to the authors, but will mean nothing to most readers.

P7543,L21-22. Please briefly clarify 'Given the lack of observations on the labile and refractory fraction of OC'. Does this mean the rates constants? Please briefly explain how Wilson et al. constrained these values. And anyway, why are constraints needed if these parameters are optimized?

Following on, are the OM degradation rate constants listed in Table 2? I see only  $R1_{opt}$  and  $R2_{opt}$ , which have units of 1/time but are described as 'rates', which has a unit of concentration/time. Please clarify this, both in the table and next to Eq. 1. Whilst on this subject, it would help the reader if units were included next to all rates/parameters in the model description (section 2.2.1).

P7545,L14. How did the cost function (Eq. 3) account for the  $NH_4$  profile? Was every data point ( $X_{model} - X_{obs}$ ) considered, or some integration of all the points together?

P7545, L17-18. I don't follow the weighting approach, please clarify. Why was the initial parameter set used?

P7545,L21-27. The authors summarize here the sensitivity analysis, but all too briefly. There are several steps mashed together in only one sentence. Please take care to explain these steps in more detail so that others can follow the logic.

P7546,L14. Please clarify that  $O_2$ ,  $NO_3$  and  $NH_4$  refer to bottom water concentrations. Please also provide the range of values used from the pelagic model in the met-model procedure. In Fig. S1, only POM flux and  $O_2$  concentrations are shown, but presumably  $NO_3$  and  $NH_4$  concentrations were also simulated, so please show them.

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P7546,L15. Suggest delete 'for each flux variable'

P7546,L19. ...to an explanatory variable *i*, and....

P7547,L8. Should 'there' be 'three'?

P7547, section 2.3. The authors should show mathematically these other different approaches, otherwise the reader has no means to judge the current model and interpret Fig. 9 and 10 (without going back to the original sources).

P7548,L20. Please explain in a bit more detail (in the model description) what permanent burial of ODU refers to.

P7550,L25. I take it that bottom water NO<sub>3</sub> and NH<sub>4</sub> concentrations are also available from the pelagic model to drive the meta-models? Please show them.

P7550,L28. 'LUMCON' means nothing to most readers. Please write out the acronym (if it is one) and add a reference if possible.

Finally, given the importance of the pelagic model results to this study, I suggest shifting Fig S1 (bottom) into the main text along with NO<sub>3</sub> and NH<sub>4</sub> concentrations which must also be available.

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