Detailed responses to review by A. Dale (reviewer comments are included in black, responses in blue font)

General comments

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.

Response: Thank you for your positive assessment. We appreciate the constructive comments and provide detailed responses below.

Specific comments

Comment:
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 O2 (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.

For instance, the NH4 flux responds almost instantaneously with POM flux in their model, but since OM does not degrade instantaneously, the NH4 flux in reality would lag behind POM flux and 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.

One assumption is to make the return flux of oxygen and nutrients a function of the instantaneous organic matter (OM) deposition flux, whereas in reality nutrients are produced and oxygen consumed as a result of OM mineralization. Instantaneous deposition flux is a good proxy for mineralization only if the OM decay rate is very high. Yet the model settings are such that 26% of OM is rather refractory, which is inconsistent with this assumption. It also means that the time-lag induced between deposition and sediment-water nutrient and oxygen fluxes is not taken into account, i.e. the memory of the sediments is ignored. Hence it is not surprising that the modeled deposition fluxes are not well suited to reproduce the measured oxygen and nutrient fluxes. It is also the reason why the modeled O2 flux follows the POM deposition so closely (P16 L12). In the recommended procedure of S2000, the sediment model dynamically describes two OM fractions (vertically integrated), and the meta model therefore prescribes the dissolved fluxes are a function of OM mineralization. The reason for choosing a reflective boundary condition, and the implications, are however not discussed in this manuscript.

Response:
We agree that the steady state assumption does not represent the memory of the sediment and thus may not be realistic in this dynamic environment. Reviewer 2 (Karline Soetaert) raised a similar concern in her comments. In order to address this problem, we decided to modify our approach using time-dependent diagenetic simulations for the derivation of the metamodel. The new method is described as follows:

P13L273-289:“ *The diagenetic model was forced with multi-year time series of bottom water conditions obtained from a biogeochemical circulation model of the Louisiana Shelf based on the Regional Ocean Modeling System (ROMS; Figure 3). The simulation is described in Fennel et al. (2013) (case B20clim) and covers the period from 2004 to 2009. The same simulation was used to prescribe POM depositional fluxes during the parameter optimization. For details on the model set up and validation we refer the reader to Fennel et al. (2013). We included only those grid cells on the Louisiana Shelf ($z < 50$ m) and west of the Mississippi River delta. Each grid cell (3791 in total) provides a time series of bottom water temperature, salinity, NO_3, NH_4, O_2 and POM depositional flux conditions that was used to run the optimized diagenetic model. We consider 2004 as a spin up year for the diagenetic model and selected the period 2005-2009 for analysis. Half of the data from each simulation were randomly chosen to derive the meta-model. The multivariate meta-model regressions were then calculated to relate bottom water conditions and depositional flux (model inputs) to the corresponding sediment-water fluxes (model output) using the $3.45 \cdot 10^6$ data vectors. To validate the meta-model we calculated correlation coefficients between the remaining data of each diagenetic model simulation (i.e. at each model grid location) and the corresponding meta-model results*.”

Figure 1, where we compare sediment-water fluxes derived from the meta-model with those predicted by a time-varying diagenetic simulation, illustrates that the new approach to deriving the meta-model can capture time-dependencies in a reasonable way. The new meta-model tracks the fluxes from the diagenetic model fairly well and is able to reproduce time-lagged responses to changes in bottom water conditions and PON deposition. Figure 2 compares the old and the new meta-models with the diagenetic model results. In the new parameterization the maxima in O_2 uptake, NH_4 efflux and NO_3 efflux all occur after the main deposition event in May, and the dependency on depositional flux is much weaker than in the old meta-model (see also the new Figure 3 below). The new meta-model is overall in much better agreement with the time-dependent diagenetic simulation.

In deriving the old parameterization we randomly sampled (in time and space) 10^5 sets of bottom water conditions from the output of a coupled circulation-biological model simulation and used these as forcing without any time dependence. In our new approach for deriving the metamodel we use the time series at each grid cell on the Louisiana Shelf from the same model simulation (3791 grid cells, 1824 days each) to force the diagenetic model. The parameterization is then calculated using half of the resulting data vectors (i.e. 3.45×10^6 vectors consisting of daily bottom water concentrations and PON deposition, as well as simulated sediment-water fluxes) from the diagenetic model simulations. The remaining data vectors are used to validate the results. Figure 1 illustrates how well the metamodel reproduces the time dependent simulation from the diagenetic model for one grid cell. We calculate the goodness-of-fit and the correlation coefficient between the diagenetic model and the metamodel parameterization for all grid cells on the Louisiana Shelf. The spatially-resolved correlation coefficients presented in Figure 4 below (Figure 6 in the revised manuscript) are above 0.8 for most of the Louisiana Shelf for O_2 and NH_4 fluxes and above 0.6 for NO_3 fluxes. The parameterization fails in some limited regions near the offshore limit of the shelf. We discuss this in the revised manuscript as follows:

P19-20L396-402: "*The spatially resolved correlation coefficients are above 0.8 for most of the Louisiana Shelf for* O_2 *and* NH_4 *fluxes and above 0.6 for* NO_3 *fluxes (Figure 6). The parameterization fails to retrieve the simulated fluxes in some limited areas near the offshore limit of the shelf. Bottom water conditions for depths greater than 50 m were not included in the meta-modeling parameterization, which explains why the meta-model does not perform well in a few limited areas along the 50 m isobath*."

We also included a more detailed discussion on the limitations of the meta-model, as suggested by the reviewer. In the Material and methods section we describe the meta-model as follows:

P13L263-271: "*Using a meta-model of sediment-water fluxes is a simplification of the method proposed by Soetaert et al. (2000) who used a meta-model of diagenetic processes (rates) instead. The aim of our technique is to combine the simplicity and efficiency of a sediment-water flux parameterization with the realism of a diagenetic model. It is important to note that our simplified meta-model is not mass conservative; however, as long as the method is used for the system for which it was developed and within the range of conditions that were used for the parameterization, violation of mass conservation should be minor. An advantage of our simplification is that it does not require knowledge of integrated POM concentration in the sediment.*"

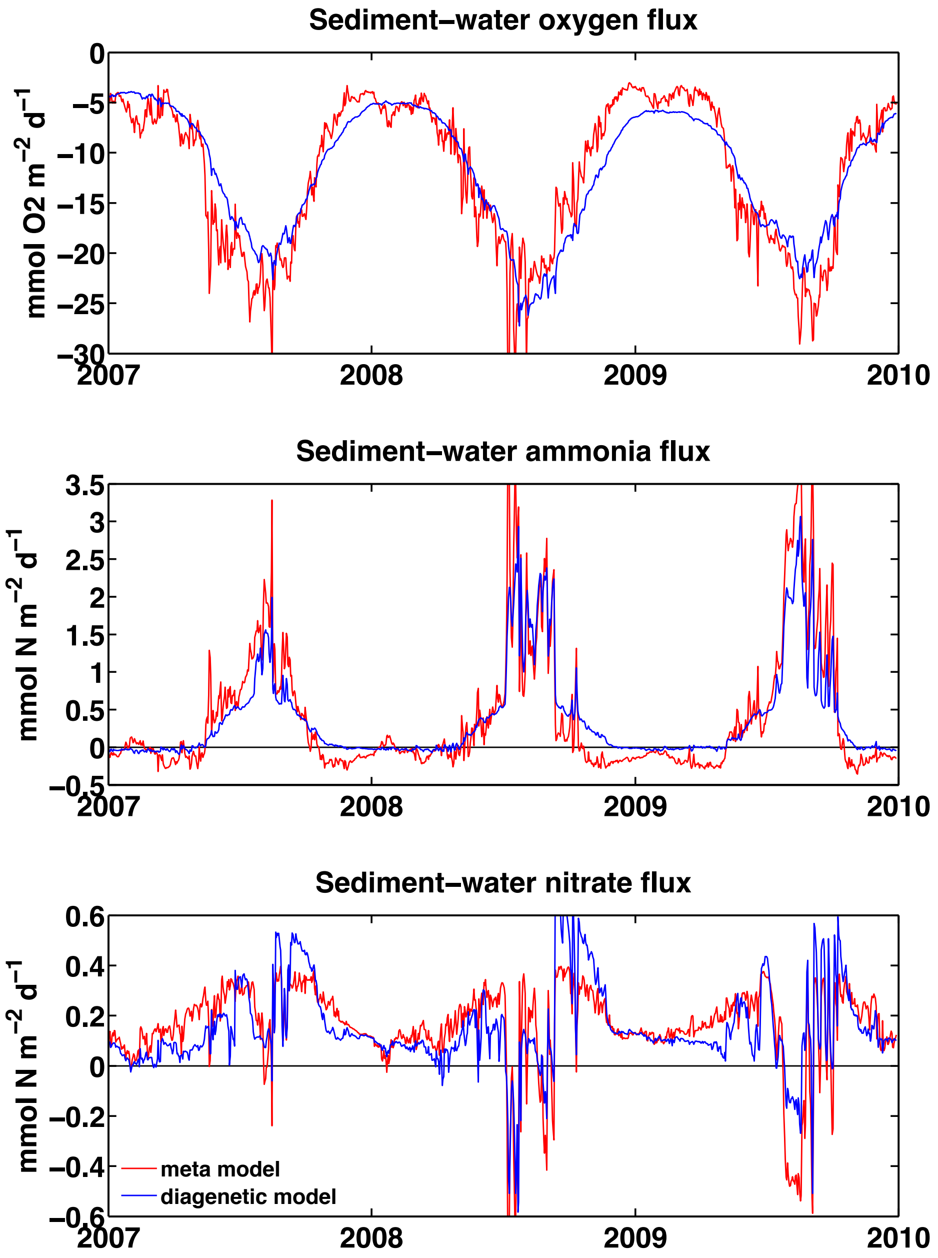

Figure 1. Time series of sediment water fluxes from a time-dependent simulation of the diagenetic model and from the new metamodel at a mid-shelf location (z=20 m, 91.5°W). The time series are used to calculate goodness-of-fit and correlation coefficients at this location, as shown in Figure 4 below. In this case correlation coefficients for O_2, NH_4 and NO_3 fluxes are 0.90, 0.93 and 0.76, respectively.

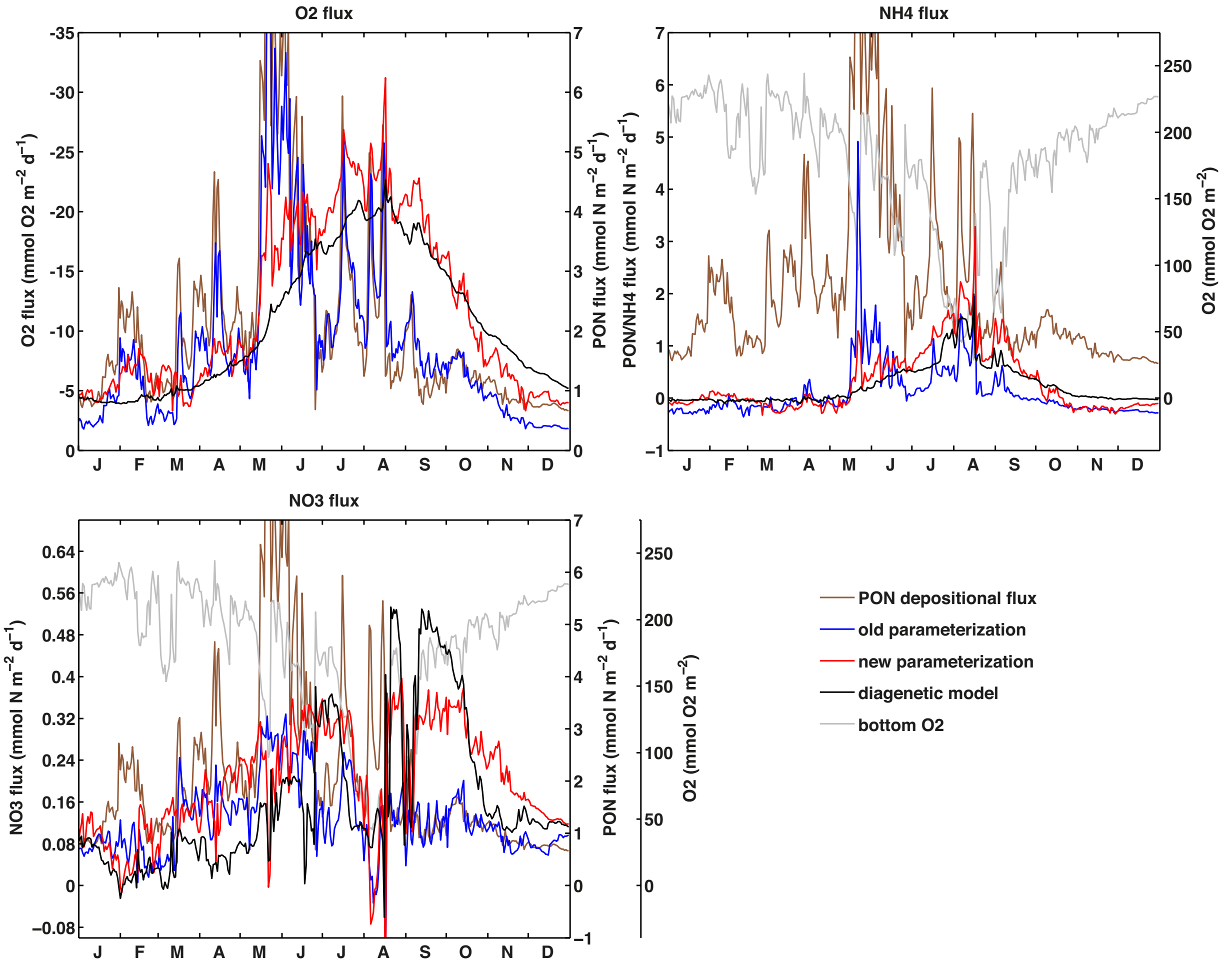

Figure 2. Comparison of sediment-water fluxes from the old metamodel (blue), the new metamodel (red) and the diagenetic model (black) at a mid-shelf location (z=20 m, 91.5°W).

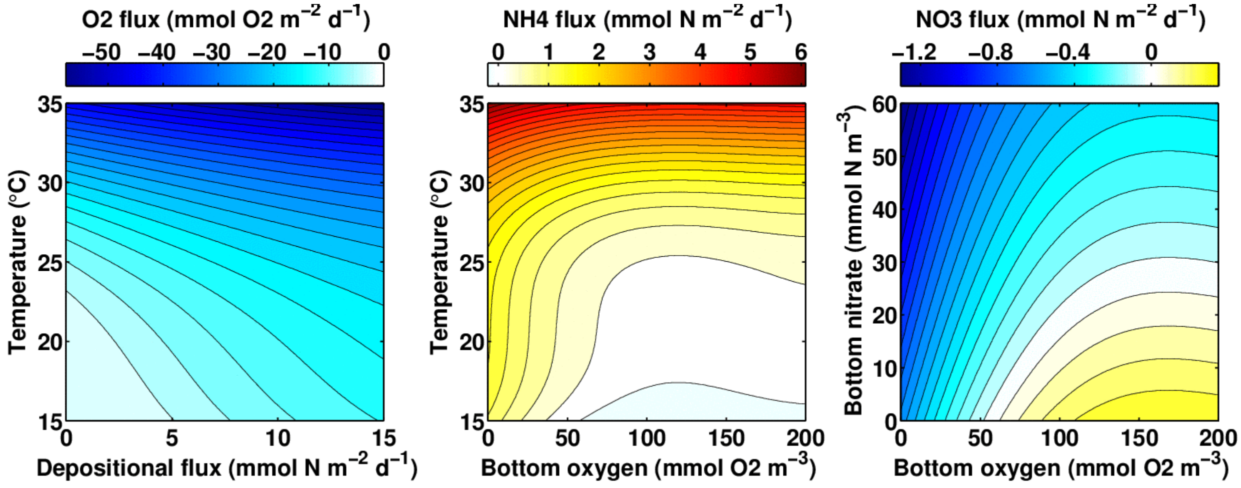

Figure 3. Updated metamodel as a function of selected drivers.

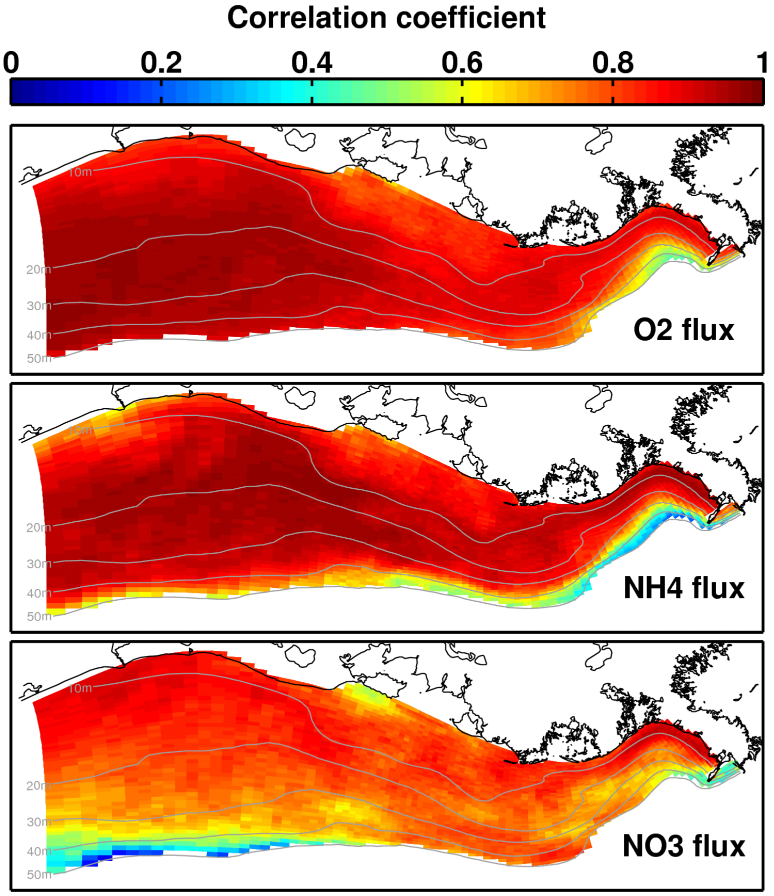

Figure 4. Correlation coefficients between time-dependent diagenetic model simulations and the parameterized fluxes for each location on the Louisiana Shelf.

Comment:
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.

Response:
We agree and we removed this statement. Unfortunately, given the limited data that we have available, we can't run the optimization in a time-dependent mode. This was not stated in the previous version of the manuscript. In the revised manuscript we explained our choice of using steady state conditions for the optimization and its implications for the meta-model as follows:

P9-10L192-198: "*The diagenetic model parameters were first optimized to match the sediment-water fluxes and sediment NH_4 concentrations observed in April, June and September 2006 at station Z02 and Z03. Since time-dependent forcing data (i.e. solute concentrations in overlying water, POM deposition) is not available for these stations we didn't run the optimization in a time-dependent mode; instead the model was run for 300 days with constant forcing for each time and location where observations were available.*"

P23-24L480-484: "*The available observations were also not sufficient to allow running the diagenetic model in a time-dependent mode and therefore the optimization was carried out with constant forcing conditions. To evaluate the effect of parameter variations (i.e. uncertainty) on the model results we carried out a sensitivity analysis on the optimized model.*"

Comment:
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 NH4 and NO3 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 NH4 concentrations and fluxes.

Response:
The monthly PON depositional fluxes in Table 1 used to force the steady state diagenetic model are averages. They represent average conditions and therefore underestimate the short-lived, high PON deposition events that occur at station Z02, as shown in Figure S1 (Figure 3 in the revised manuscript). Given the lack of PON depositional flux data, and therefore the high uncertainty on PON deposition, we chose to use average fluxes to force the steady state diagenetic model. We clarified this choice as follows:

P10L199-203: "*Since no observations of POM depositional flux were available, POM depositional fluxes were prescribed using monthly means calculated for station Z02 and Z03 from a multiyear biogeochemical model simulation (see Section 2.2.3). The mean depositional* *fluxes do not represent short-lived deposition events which is appropriate for a model with constant forcing*."

This is a limitation to our optimization that we discuss more extensively in the revised manuscript:

P23-24L483-489: "*To evaluate the effect of parameter variations (i.e. uncertainty) on the model results we carried out a sensitivity analysis on the optimized model. A key driver of diagenetic processes is POM deposition and the remineralization of the labile deposited POM is the most sensitive parameter in the model. Observations of POM deposition were not available and using average rates of POM deposition from a biogeochemical model, as we have done here, is an additional source of uncertainty. This is demonstrated by the improved agreement between simulated and observed sediment-water fluxes when including POM deposition in the optimization*."

Comment:
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 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?

Response:
The evolutionary algorithm explores the parameter space by adding random noise and is therefore less prone to finding local minima than the widely used gradient-descend algorithms (see also response to Comment 3 by Reviewer 2). Nonetheless the evolutionary algorithm technique may be sensitive to the initial set of parameter values (Schartau and Oschlies, 2003). We repeated the optimization procedure with different initial parameter sets and found that the end result was not sensitive to the initial parameter choice.

Comment:
5. POC fluxes in this system are high (>100 mmol/m2/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 ($NO_3 + H_2S \rightarrow NH_4 + SO_4$). 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 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 NO3 uptake by bacteria may also explain why the diagenetic and meta-models are unable to simulate high NO3 fluxes (Fig. 2 and Fig. 5c).

Response:
We would first like to note that hypoxia at station Z02 is not severe for extended periods of time. Figure 3 in the revised manuscript shows that hypoxia is mild in July and severe only for a brief period in August at station Z02. Figure S2 (Figure 12 in the revised manuscript), which was cited by the reviewer, does not show oxygen concentrations. High porewater sulfide concentrations near the sediment-water interface are not reported for sediments on the Louisiana Shelf (Morse and Eldridge, 2007; Morse and Lin, 1991).

We added a paragraph in the revised manuscript to discuss the limitations of the diagenetic model and the potential effects of the omission of DNRA on our results. Overall, there is a relatively poor understanding of the importance of DNRA on the Louisiana shelf due to a lack of observations in the region (Dagg et al., 2007). Nunnally et al. (2013) suggested the occurrence of DNRA given observed nitrate depletion in bottom water samples. In a recent study, McCarthy et al. (2015) didn't find DNRA to be a consistent N pathway on the Louisiana Shelf; however, they recommend further investigation of this process. Given the lack of consensus on DNRA in our region we didn't include this process in the diagenetic model recognizing that this is a potential shortcoming of the diagenetic model. We discussed this issue as follows in the revised manuscript (see also our response to Comment 5 by Reviewer 2):

P24L498-512: "*Some mismatch between model and observations may also be generated by missing processes in the diagenetic model. As in earlier studies of the Louisiana Shelf (Morse and Eldridge, 2007; Eldridge and Morse, 2008), the diagenetic model does not represent DNRA and anammox. Although DNRA can be an important contributor to the N cycle under severe hypoxia (Dale et al., 2013), there is a poor understanding of the importance of DNRA on the Louisiana Shelf due to the lack of observations (Dagg et al., 2007). High porewater sulphide concentrations near the sediment-water interface are not reported for sediments of the Louisiana Shelf (Lin and Morse, 1991; Morse and Eldridge, 2007), which tend to minimize the importance of DNRA. However, the large* NH_4 *porewater concentrations observed at station Z02 in September (Figure 2) could be explained by the occurrence of DNRA. Anammox may also be a sink for bottom water* NH_4 *on the Louisiana Shelf (Lin et al., 2011). McCarthy et al. (2015) found that anammox may represent, at times, up to 30% of denitrification (including anammox) in some locations of the Louisiana Shelf. As a result,* NH_4 *flux to the water column may be overestimated by the diagenetic model, and in the parameterization, under low bottom* O_2 *conditions.*"

P25L516-518: "*Further development of the diagenetic model may include explicit anaerobic reactions, including DNRA and anammox. However, this is beyond the scope of this work.*"

Comment:
6. Similarly, given the severe depletion of O2 in late summer, one could expect infaunal mixing by bioturbation and bioirrigation to be dependent on O2, in line with other observations and models (Dale et al., 2013). Please comment.

Response:

The optimization tends to minimize the influence of bioturbation in the diagenetic model (depth of bioturbated layer, non-local mixing). This likely reflects the effect of hypoxia on the sediment biota and is in line with observations from the Louisiana Shelf, which show that bacteria tend to dominate the sediment community. Given the limited information on the relationship between porewater O_2, infauna biomass and irrigation in this region (Eldridge and Morse, 2008), we assumed that bioturbating macrobiota does not re-establish itself in the regions affected by recurring severe seasonal hypoxia or anoxia, thus we do not expect a strong dependence of bioturbation and bioirrigation on O_2 in this system. We discuss this in the Discussion section, and we now comment on this assumption in the description of the diagenetic model (section 2.2.1) in the revised manuscript as follows:

P8L163-170: "*Bioturbation and non-local mixing of solutes are not dependent on O_2 in the model. Such a dependence could be introduced to account for repeated cycles of eradication/re-establishment of macrofauna due to anoxia. However, given the limited information on the relationship between porewater O_2, infauna biomass and irrigation in this region (Eldridge and Morse, 2008), we assumed that macrobiota does not re-establish itself in the regions affected by recurring severe seasonal hypoxia or anoxia on the Louisiana Shelf and thus do not expect a strong dependence of bioturbation and bioirrigation on O_2.*"

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

Response:
Temperature influences the solute diffusivity and the degradability of reactive and refractory organic matter in the diagenetic model. Bioturbation diffusivity is also temperature-dependent. We clarified the role of temperature in the revised description of the diagenetic model (section 2.2.1) as follows:

P7-8L150-156: "*In the updated model temperature thus influences the solute diffusivity, the degradability of the two OM pools and bioturbation. This modification allows for the representation of temperature-dependence of microbial processes in the sediment (aerobic respiration, denitrification and anaerobic metabolism), which is known to be important in coastal systems (see, e.g., Fig. 5 in Wilson et al. 2013). Nitrification is not temperature dependent in the diagenetic model. It is assumed that O_2 concentration is the main factor limiting nitrification in the Louisiana Shelf sediments.*"

Comment:
8. The meta model predicts a high O2 flux at zero O2 bottom water concentrations (Fig. 9a). This is strange and must be clarified.

Response:
O_2 flux at zero O_2 bottom waters represents the production of ODUs under anaerobic conditions; we assume that ODUs are oxidized instantaneously in the water column and therefore the total O_2 flux represents an O_2 consumption by the sediment. This is explained in the Discussion section as follows:

P27-28L560-579: "*Perhaps a key difference to other sediment-water parameterizations is the importance of ODU at low O_2, which results in a relatively weak relationship between O_2 flux and bottom O_2 concentration in hypoxic conditions, and the occurrence of O_2 flux in anoxic conditions; in the meta-model, ODU is the dominant source of O_2 consumption in hypoxic conditions and at high temperature (i.e., in summer), independently of bottom O_2 concentration. Previous parameterizations of sediment-water O_2 flux on the Louisiana Shelf considered only SOC and therefore O_2 flux decreased toward zero with decreasing bottom O_2 in the hypoxic range (with a zero intercept for anoxic conditions). However, Lehrter et al. (2012) found an increase of the DIC/O_2 flux ratio with bottom O_2 depletion that they attributed to anaerobic metabolism, i.e. the production of reduced chemical species that accumulate in the sediment, diffuse back and reoxidize in the water column when O_2 becomes available. Justić and Wang (2014) considered the effect of reduced chemical species on biological oxygen demand in their hypoxia model. It represents a significant O_2 sink in bottom waters and needs to be accounted for in the sediment-water O_2 flux parameterization. The O_2 flux meta-model combines SOC and ODU fluxes and is therefore a more realistic representation of O_2 consumption at the sediment-water interface. This formulation assumes instant ODU oxidation in the water column, even in anoxic conditions, whereas oxidation occurs in oxygenated waters only. The time delay between ODU flux and oxidization is therefore missing in the meta-model but is accounted for if the coupled biogeochemical-circulation model carries an O_2 debt in anoxic conditions, as is the case in the models of Fennel et al. (2009, 2013) and Laurent and Fennel (2014).*"

We also added the following in the Results section:

P22-22L448-453: "*O_2 flux decreases at low bottom water O_2 concentration but does not stop in anoxic conditions, as it is the case for H&D and M&L. At low O_2, ODUs become the dominant O_2 sink (due to ODU oxidation in the water column) and therefore the O_2 sink can be significant despite the lack of O_2 in bottom waters*"

Comment:
9. Can the authors explain why the NO3 flux does not depend at all on POM flux (Table 4). After all, no POM = no diagenesis.

Response:
The dependence of NO_3 flux on POM deposition has changed in the updated metamodel, which is now able to capture time-lagged effects on NO_3 fluxes. NO_3 flux is strongly dependent on the presence of O_2 in bottom waters, as shown in Figures 2 and 3 above.

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

Response:
The figures were updated with larger font sizes.

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

Response:

In section 2.1 we mention that the two stations are along the 20m isobath, as shown in Figure 1. We feel that including the water depths in Table 1 would be redundant.

Comment:
12. Table 1 header. I believe that the fluxes and NH4 profiles are used to optimize the diagenetic model via Eq. 3, not the boundary conditions listed in this table.

Response:
The boundary conditions listed in Table 1 are used as boundary conditions for the diagenetic model. Fluxes and NH_4 profiles are used to calculate the cost in the optimization procedure. We clarified the header in Table 1 as follows: "*These data are used as boundary conditions during the optimization of the diagenetic model*".

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

Response:
We clarified that point by adding the following sentence to Table 4 header (P39L823-827): "*A positive effect promotes a weaker flux into the sediment or a larger flux to the water column (depending on the direction of the flux) whereas a negative effect leads to a larger sink into the sediment or a weaker flux to the water column. +/– indicates that the effect's direction varies as a function of the variable.*"

Comment:
14. P7538,L13 and P7540,L40. ...O2, NO3 and NH4 fluxes. P7539,L19 nitrate/nitrite.

Response:
The text was modified accordingly.

Comment:
15. 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).

Response:
The text and references were modified accordingly.

Comment:
16. 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).

Response:
Vertically integrated model refers to a single layer model of diagenesis. In the sentence P3L64 we removed "*Vertically integrated or depth-resolved*" and now we refer to *mechanistic models* instead.

Comment:
17. I would personally like to see, for the sake of correctness, charges assigned to the anions, (e.g. NH4+ instead of NH4). But that's just my own preference.

Response:
The text was modified accordingly.

Comment:
18. 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 large number of observations were made.

Response:
We added more methodological information on sediment-water flux observations in Section 2.1. The observations are now described as follows:

P6L113-118: "*On each date, eight sediment cores were collected at each station (3 for O_2 flux, 3 for nutrient fluxes and 2 for sediment profiles). O_2 and nutrient fluxes were measured on site from triplicate individual incubations in sediment chambers. Sediment NH_4 concentration was measured for each 2 cm bin in the duplicate sediment cores. Bottom water temperature and salinity were measured with a CTD, whereas O_2 and nutrient concentrations were measured in the water overlying the sediment cores.*"

Comment:
19. 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.

Response:
The text was modified accordingly. We also replaced "*near shelf survey stations X*" by "*see Murrell et al., 2013, for details on sampling design*".

Comment:
20. 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?

Response:
The diagenetic model divides OC into labile and refractory pools. There are no direct observations available for our sites. We assumed that the fraction of deposited OC that is labile is constant in our experiments. Since deposited OC mainly originates from local primary production, we assumed that labile OC makes up 74% ($OC_{frac2} = 0.74$), as in Wilson et al (2013). The fraction of labile and refractory material in deposited OC is part of the model forcing and we chose to not make it part of the optimized parameter set. In the revised manuscript we excluded OC_{frac2} from the parameter list in Table 2 and instead described it with the diagenetic model (section 2.2.1). We also clarified our choice and the underlying assumptions by adding the following:

P9L176-183: "*Since deposited OC mainly originates from local primary production on the shallow Louisiana Shelf (Redalje et al., 1994; Justić et al., 1996; Rowe and Chapman, 2002), labile OC is assumed to represent 74% of total OC in deposited material. This value was used by Soetaert et al. (1996a) to represent the fraction of labile organic matter in surface waters and is in line with previous modeling investigations of the Louisiana Shelf (Justić et al., 1996; Eldridge and Morse, 2008). However, inshore areas adjacent to river discharge may have higher fraction of terrestrial organic matter.*"

Comment:
21. Are the OM degradation rate constants listed in Table 2? I see only R1opt and R2opt, 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).

Response:
In Table 2 and in the text we now refer to "*remineralization*" rather than "*remineralization rate*" since R_1^{Topt} and R_2^{Topt} have units of 1/time. We also provide units next to the parameters in section 2.2.1, as suggested by the reviewer.

Comment:
22. P7545,L14. How did the cost function (Eq. 3) account for the NH4 profile? Was every data point (Xmodel – Xobs) considered, or some integration of all the points together?

Response:
In order to avoid a biasing toward profiles in the cost calculation we compute an average cost per profile. This information was added to the revised manuscript as follows:

P12L249-250: "*To avoid biasing the cost calculation toward NH_4 profiles we computed an average cost per profile*."

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

Response:
Without weighting, the contribution to the total cost from O_2, NH_4 and NO_3 sediment-water fluxes and NH_4 profiles would be quite different despite the presence of the standard deviation in the denominator of the cost function terms. This is common when different data types are combined into one total cost and reflects the fact that models have an easier time fitting some data types than others. We chose the weights in order to ensure that all data types contribute about equally to the cost function initially. The initial parameter set is used to estimate the weights. We clarified the weighting approach in the revised manuscript by adding the following:

P12L246-249: "*The weight gives the variables approximately equal influence on the overall cost, at least initially. The weighting approach is common in parameter optimization studies (see, e.g., Friedrichs, 2001; Schartau and Oschlies, 2003; Friedrichs et al., 2007; Kane et al., 2011).*"

Comment:

24. 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.

Response:

We extended and clarified the description of the sensitivity analysis in the revised manuscript describing each step, as follows:

P18-19L371-390: "*For most of the parameter set, the optimized model is insensitive to parameter variation (Figure 5). The most sensitive process in the diagenetic model is the remineralization of the fast decaying organic matter pool, since the optimized model is sensitive to all the associated parameters, namely the remineralization of the fast decaying organic matter pool ($R_2(T)$), the base temperature (T_b) and the Q_{10} factor for fast decaying organic matter (θ_{r1}) in the Q_{10} relationship. The optimized model is also sensitive to the variation in POM deposition rates at station Z03 (F_{POM3x}), mainly in June. Variation in deposition rates at station Z02, however, does not influence the overall cost. The sensitivity to parameters or model forcing related to organic matter is not surprizing given the high magnitude and large temporal and spatial variations in POM deposition in this region. Nonetheless, it highlights the overall uncertainty in the optimized model due to the lack of observations on depositional flux. The difference in sensitivities to the depositional flux at stations Z02 and Z03 can be explained by the magnitude of the total cost, which is higher at station Z03 (Table 3). The cost at station Z02 is sensitive to the POM deposition rate (e.g. >300% increase in April), but since the cost at station Z03 is much higher, the effect on the total cost is small. The uncertainty associated with POM deposition rates is then larger at station Z03. To a lesser extent, the optimized model is sensitive to the bioturbation diffusivity (D_{bio0}) and to the maximum rate of nitrification (Nit). The cost is largest for NO_3 flux (Table 3), which indicates that the optimization has more difficulty fitting the observations for this flux. The sensitivity of the optimized value for nitrification rate, which influence NO_3 flux, is therefore higher.*"

Comment:

25. P7546,L14. Please clarify that O2, NO3 and NH4 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 O2 concentrations are shown, but presumably NO3 and NH4 concentrations were also simulated, so please show them.

Response:

This paragraph was modified and now includes the following (P13L280-282): "*Each grid cell (3791 in total) provides a time series of bottom water temperature, salinity, NO_3, NH_4, O_2 and POM depositional flux conditions that was used to run the optimized diagenetic model*". Also, we now provide the range of values for each variable used in the metamodel in Table 4. NH_4 and NO_3 were also added to the revised supplementary Figure S1 (Figure 3 in the revised manuscript).

Comment:

26. P7546,L15. Suggest delete 'for each flux variable'. P7546,L19. ...to an explanatory variable i, and... P7547,L8. Should 'there' be 'three'?

Response:

The text was modified accordingly.

Comment:
27. 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).

Response:
The formulations of each parameterization were added to section 2.3. (see P14-15L300-310).

Comment:
28. P7545 P7548,L20. Please explain in a bit more detail (in the model description) what permanent burial of ODU refers to.

Response:
We included the following in the model description:

P7L137-139: "*The burial of ODU refers to the deposition of ODUs as solids (e.g., pyrite, manganese carbonate) below the bioturbated zone (Soetaert et al., 1996a).*"

Comment:
29. P7550,L25. I take it that bottom water NO3 and NH4 concentrations are also available from the pelagic model to drive the meta-models? Please show them.

Response:
Bottom water NO_3 and NH_4 at station Z02 and Z03 were included in Figure S1 (Figure 3 in the revised manuscript).

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

Response:
We now present spatial snapshots on August 15th, 2009 that better display the effect on hypoxic conditions on sediment-water fluxes and the decoupling between POM deposition and sediment-water fluxes in mid summer. Therefore, in the revised manuscript we removed the reference to the LUMCON cruise.

Comment:
31. Finally, given the importance of the pelagic model results to this study, i suggest shifting Fig S1 (bottom) into the main text along with NO3 and NH4 concentrations which must also be available.

Response:
Figure S1 was moved to the main text and is now Figure 3. We also moved Figure S2 to the main text. Figure S2 is now Figure 12.

References:

Dagg, M., Ammerman, J., Amon, R., Gardner, W., Green, R. and Lohrenz, S.: A review of water column processes influencing hypoxia in the northern Gulf of Mexico, Estuaries Coasts, 30(5), doi:10.1007/BF02841331, 735–752, 2007.

McCarthy, M. J., Newell, S. E., Carini, S. a. and Gardner, W. S.: Denitrification Dominates Sediment Nitrogen Removal and Is Enhanced by Bottom-Water Hypoxia in the Northern Gulf of Mexico, Estuaries and Coasts, doi:10.1007/s12237-015-9964-0, 2015.

Morse, J. W. and Eldridge, P. M.: A non-steady state diagenetic model for changes in sediment biogeochemistry in response to seasonally hypoxic/anoxic conditions in the “dead zone” of the Louisiana shelf, Mar. Chem., 106(1-2), 239–255, doi:10.1016/j.marchem.2006.02.003, 2007.

Lin, S. and Morse, J. W.: Sulfate reduction and iron sulfide mineral formation in Gulf of Mexico anoxic sediments, Am. J. Sci., 291(1), 55–89, doi:10.2475/ajs.291.1.55, 1991.

Nunnally, C. C., Rowe, G. T., Thornton, D. C. O. and Quigg, A.: Sedimentary Oxygen Consumption and Nutrient Regeneration in the Northern Gulf of Mexico Hypoxic Zone, J. Coast. Res., 63, 84–96, doi:10.2112/SI63-008.1, 2013.

Schartau, M. and Oschlies, A.: Simultaneous data-based optimization of a 1D-ecosystem model at three locations in the North Atlantic: Part I—Method and parameter estimates, J. Mar. Res., 61(6), 765–793, doi:10.1357/002224003322981147, 2003.

Detailed responses to review by K. Soetaert (reviewer comments are included in black, responses in blue font)

General comments

As the method is of use for a broad audience, and it is suitable for the journal, I would recommend publication, albeit after major revision. One of the flaws of the current manuscript is that the reasons and consequences of the deviations of the approach from S2000 are not at all discussed.

Response: We appreciate the careful and critical comments. We have made an effort to improve upon the assumption of steady state, which was raised as a shortcoming by both reviewers. We also better discuss the limitations of our approach in the revised manuscript.

Specific comments

Comment:
1. One assumption is to make the return flux of oxygen and nutrients a function of the instantaneous organic matter (OM) deposition flux, whereas in reality nutrients are produced and oxygen consumed as a result of OM mineralization. Instantaneous deposition flux is a good proxy for mineralization only if the OM decay rate is very high. Yet the model settings are such that 26% of OM is rather refractory, which is inconsistent with this assumption. It also means that the time-lag induced between deposition and sediment-water nutrient and oxygen fluxes is not taken into account, i.e. the memory of the sediments is ignored. Hence it is not surprising that the modeled deposition fluxes are not well suited to reproduce the measured oxygen and nutrient fluxes. It is also the reason why the modeled O2 flux follows the POM deposition so closely (P16 L12). In the recommended procedure of S2000, the sediment model dynamically describes two OM fractions (vertically integrated), and the meta model therefore prescribes the dissolved fluxes are a function of OM mineralization. The reason for choosing a reflective boundary condition, and the implications, are however not discussed in this manuscript.

Response:
In response to this concern (also Comment 1 by Reviewer 1, Andy Dale), we modified the diagenetic model used in the meta-model derivation. Instead of steady state we now use dynamic forcing for the diagenetic model. Figure 2 (given in our response to Reviewer 1) shows how our original meta-model (based on steady state forcing) fails to capture the temporal evolution of sediment-water fluxes from a time-varying diagenetic simulation (consistent with the concern raised by both reviewers). Figure 2 also shows how our modified procedure using time-dependent simulations in the derivation of the meta-model results in a parameterization that is much better able to reproduce the temporal evolution of the fluxes. The updated diagenetic model accounts for the memory of the sediment, although not in a mechanistic way. The decoupling between PON deposition and O_2 flux in the revised meta-model is obvious in Figure 2. The updated meta-model remains simpler than the procedure recommended in S2000. We introduced the new meta-modeling procedure and discussed the implications and potential limitations of our choice in the revised manuscript as follows:

P13-14L263-289: "*Using a meta-model of sediment-water fluxes is a simplification of the method proposed by Soetaert et al. (2000) who used a meta-model of diagenetic processes (rates) instead. The aim of our technique is to combine the simplicity and efficiency of a sediment-water flux parameterization with the realism of a diagenetic model. It is important to note that our simplified meta-model is not mass conservative; however, as long as the method is used for the system for which it was developed and within the range of conditions that were used for the parameterization, violation of mass conservation should be minor. An advantage of our simplification is that it does not require knowledge of integrated POM concentration in the sediment.*

In order to obtain the meta-model parameterization the diagenetic model was run many times in time-varying mode using the single parameter set optimized for the Louisiana Shelf. The diagenetic model was forced with multi-year time series of bottom water conditions obtained from a biogeochemical circulation model of the Louisiana Shelf based on the Regional Ocean Modeling System (ROMS; Figure 3). The simulation is described in Fennel et al. (2013) (case B20clim) and covers the period from 2004 to 2009. The same simulation was used to prescribe POM depositional fluxes during the parameter optimization. For details on the model set up and validation we refer the reader to Fennel et al. (2013). We included only those grid cells on the Louisiana Shelf ($z < 50$ m) and west of the Mississippi River delta. Each grid cell (3791 in total) provides a time series of bottom water temperature, salinity, NO_3, NH_4, O_2 and POM depositional flux conditions that was used to run the optimized diagenetic model. We consider 2004 as a spin up year for the diagenetic model and selected the period 2005-2009 for analysis. Half of the data from each simulation were randomly chosen to derive the meta-model. The multivariate meta-model regressions were then calculated to relate bottom water conditions and depositional flux (model inputs) to the corresponding sediment-water fluxes (model output) using the $3.45 \cdot 10^6$ data vectors. To validate the meta-model we calculated correlation coefficients between the remaining data of each diagenetic model simulation (i.e. at each model grid location) and the corresponding meta-model results."

P27L551-555: "*This simplified parameterization method does not require an additional, vertically-integrated sediment layer to track deposited POM as in the method proposed by Soetaert et al. (2000). Although the meta-model is not mass conservative, violation of mass conservation should be minor if the meta-model is used for the system and within the range of conditions that were used for its development.*"

P29L606-609: "*Soetaert et al. (2000) proposed an intermediate method to improve the efficiency of benthic-pelagic coupling in biogeochemical circulation models. Here we presented a simplified version computing a meta-model of sediment-water fluxes for use in a regional biogeochemical model through optimization of a diagenetic model*"

Comment:
2. The 'novelty' of the method is that the metamodel directly fits the oxygen, nitrate and ammonium fluxes as a function of the water-column conditions. In contrast, in the S2000 paper, the fraction nitrified, denitrified and anoxic mineralized is fitted instead, and the fluxes derived from the mineralization rates. The reason for this choice was that this is mass conservative. Deviating from this as in the current manuscript, it is well possible that, due to statistical fitting, for instance more nitrogen is returned than is originally deposited in the sediment – which means that mass is numerically created. This may not be the case, but at least the authors should spend a

paragraph as to why they decided to do the meta-modeling differently and whether or not mass is (numerically) created by doing this.

Response:

We agree that our parameterization is not mass conservative. An accounting of organic matter in the sediment would be necessary to implement the mass-conserving option recommended in S2000. In this case we chose the simplest approach to provide more realistic sediment-water fluxes than have been used in the past in regional biogeochemical models for the Louisiana Shelf. As long as the metamodel is used for the system for which it was developed and within the range of conditions that were used for the parameterization, violation of mass conservation should be minor. We agree that these limitations and caveats have to be clearly stated. We now provide more discussion of the assumptions, the mass balance issue and the limitations of our method in the revised manuscript. The modifications in the revised manuscript are detailed in the response to Comment 1 above.

Comment:

3. I have strong doubts on the statistical validity of the fitting procedure. In my experience, it is not possible to find robust estimates of the 20 parameters that were selected, given the small amount of data available. To be able to fit all these parameters, it is necessary that they are 'identifiable', i.e. the value of one parameter does not depend to a large extent on the values of (a set of) the other parameters. Parameters that are not identifiable by the data, have very large uncertainty. Unfortunately, the genetic algorithm does not return a measure of parameter uncertainty. A very old paper of mine deals with the identifiability of a diagenetic model (http://dx.doi.org/10.1357/002224098321822401); a more recent paper presents software to do more robust parameter fitting that includes a.o. estimating parameter identifiability, parameter sensitivity, and to evaluate the uncertainty of the derived parameters. (www.jstatsoft.org/v33/i03/paper). I realize that it would be too much of an effort to require all this now, but at least the lack of statistical rigor should be mentioned in the manuscript and the results discussed in section P12-L13 and on P18-L25 should be phrased less strongly.

Response:

We expanded the presentation of the fitting procedure and mention the identifiability issue (including the two references provided by the reviewer). However, we note that the issue of poor identifiability of certain parameters would not be alleviated by using a different optimization approach (assuming that different approaches find the same optimum). The only real solution to the issue would be to have a more complete set of observations to optimize against. We discuss this as follows in the revised manuscript:

P23L475-480: "*An issue with the optimization of large parameter sets in diagenetic models is the poor identifiability of some parameters that results in a large uncertainty in their value (Soetaert et al., 1998). This caveat in our optimization approach would not be alleviated by using a different type of optimization. Several methods have been proposed to estimate parameter identifiability and uncertainty (Soetaert et al., 1998; Soetaert and Petzoldt, 2010, Fennel et al. 2001). However, a more complete set of observations would be necessary.*"

The genetic algorithm is a well-accepted method for optimization problems in the statistical literature (Chatterjee et al., 1996; Fogel, 1994; Hibbert, 1993; Kolda et al., 2003). This technique has been increasingly used to optimize parameters in biogeochemical models of the water column (Schartau and Oschlies, 2003; Robson et al., 2008; Ward et al., 2010; Kuhn et al., 2015) and the sediment (Wilson et al., 2013; Wood et al., 2013). An advantage of the evolutionary algorithm over the traditionally more common gradient-descend algorithms is that it explores the parameters space with an element of randomness and therefore is less prone to converging on a local minimum. In addition to the optimization, we carried out a sensitivity analysis of the parameter set to explore the effect of parameter change ("uncertainty") on the model results. We improved the discussion on this issue in the revised manuscript as follows:

P10L206-218: "*The evolutionary algorithm is a well accepted method for optimization problems (Hibbert, 1993; Fogel, 1994; Chatterjee et al., 1996; Kolda et al., 2003) and has been increasingly used to optimize parameters in biogeochemical models (Kuhn et al., 2015; Robson et al., 2008; Schartau and Oschlies, 2003; Ward et al., 2010). The technique was successfully used for the optimization of parameters of Soetaert et al.'s (1996a) diagenetic model in two independent studies (Wilson et al., 2013; Wood et al., 2013). The advantage of the evolutionary algorithm over traditionally used gradient-descent algorithms is that it explores the parameter space with an element of randomness and therefore is less prone to converging on a local minimum. Each parameter is given a range of variation within which the algorithm will search for the best value to match the observations. Regardless of which minimization technique is used, gradient-descent or an evolutionary algorithm, some parameters may not be identifiable because they are unconstrained by the available observations (Soetaert et al., 1998; Fennel et al., 2001).*"

Comment:
4. From table 2, it is clear that the modeled sediment depth is only 10 cm. Given the boundary conditions that are imposed on the diagenetic model, this entails that gradients vanish at that depth (which is seen on the modeled ammonium profiles in Fig. 2). However, the observations, especially in April and one profile in September still show a large gradient at 8 cm; this makes me suspect that restricting the model to the upper 10 cm of sediment is not adequate for these data.

Response:
We acknowledge that restricting the diagenetic model to the upper 10 cm is a limitation. We mention this limitation as follows in the revised manuscript:

P16-17L331-333: "*Some of the observed NH_4 profiles in April and September display a gradient at depth (Figure 2) and therefore the 10 cm deep diagenetic model might not be able to resolve.*"

Comment:
5. The OMEXDIA model would need a few other additions to make it better suitable for these high-flux sediments (e.g. a reaction of ODU and NO3).

Response:
While further modification of the diagenetic model is beyond the scope of the present manuscript, we would be most appreciative of further guidance on how the model can be improved for the region. We now suggest some additions to the diagenetic model in the revised manuscript (see response to Comment 5 by Reviewer 1). The main focus of this manuscript is to present a method for parameterizing sediment-water fluxes and apply it to the Louisiana Shelf.

Comment:
6. Salinity is a parameter inputted to the meta-model, but it is unclear how it influences the diagenetic model.

Response:
Salinity is not used in the diagenetic model so the values in Table 1 are only informative of bottom water conditions. We removed salinity from Table 1 to avoid confusion.

Comment:
7. Fig. 2. The original OMEXDIA model would never be able to generate the steady-state ammonium profiles from April. As ammonium peaks at 3 cm, it means that there is a sink of ammonium below that depth, although there is no oxygen. What causes this decline?

Response:
We reviewed the optimized steady state model results from April and ruled out the presence of a deep ammonium sink at steady state. However we noticed that the optimized simulations for April didn't reach a full steady state at depth, which resulted in the negative gradient in the deep layers. This is stated as follows in the revised manuscript:

P16L333-335: "*There is also a deep negative gradient in the simulated profiles in April indicating that the model didn't reach full steady state conditions at depth. However, this mismatch at depth has a limited effect on sediment-water fluxes*".

We also mention P10L197 that the model ran with constant forcing for 300 days.

Comment:
8. Fig. 9. The oxygen flux is negative everywhere except in this figure. Should be made consistent. Equation (1) Topt is not a good name for this parameter; the term 'optimal' suggest that the function peaks at the temperature, which it does not. Topt is the "base" temperature, i.e. the temperature for which the rate is defined. Usually the base temperature is taken as 0 degrees or 20 degrees. It would be easier to compare the derived rates with those from other models if using a more standard base temperature (rather than 30 degrees).

Response:
For consistency we made the O_2 flux negative in Figure 9 (Figure 10 in the revised manuscript). We also changed T_{opt} to T_b for base temperature throughout the revised manuscript.

Comment:
9. Equation (2). Give the units of I(z).

Response:
The units of I(z), μmol L^{-1} y^{-1}, were added to the revised manuscript. In the revised manuscript we also provide the units next to each parameter in the text (see Comment 21 by Reviewer 1).

Comment:
10. Equation (3):

*why is it sigma (s,i) and not sigma(s,t,i).

*I do not understand the meaning of 1/wi – this weighing is not standard and seemingly dependent on an –arbitrary- initial parameter set? Due to the division by the standard deviation, the fact that units are different is already taken into account, so I so not see the need to have an extra weighing term.

*How does the variable cost in Table 3 relate to formula (3)-does it include the 1/wi term?

Response:
We corrected to $\sigma^2_{s,t,i}$.

We clarified the weighting approach in the revised manuscript (see also response to Comment 26 by Reviewer 1). A weight was included in the cost function to prevent that some variables have more influence on the overall cost than others, at least initially. The weighting is common in parameter optimization studies (see, e.g., Friedrichs, 2001; Friedrichs et al., 2007; Kane et al., 2011; Schartau and Oschlies, 2003). By using the initial parameter set in estimating the weights prior to optimization we ensure that all data types initially contribute equally to the optimization. We added the following in the description of the parameter optimization (Section 2.2.2):

P12L246-250: "*The weight gives the variables approximately equal influence on the overall cost, at least initially. The weighting approach is common in parameter optimization studies (see, e.g., Friedrichs, 2001; Schartau and Oschlies, 2003; Friedrichs et al., 2007; Kane et al., 2011). To avoid biasing the cost calculation toward the* NH_4 *profiles we computed an average cost per profile.*"

The values in Table 3 correspond to the cost function *F* given in Equation 3 (including the weights).

Comment:
11. Table 2.

*Units of aNH3, aO2, etc.. and the unit of kinanox are wrong.

*Unit of Dbcoeff and PB is lacking; also the NC ratio has a unit: is it gram/gram or mol/mol?

*A lot of the optimized parameter values are rather round numbers, which make me assume that they are located somewhere near the edge of the allowed range? What was the range imposed?

Response:
In the revised Table 2 we modified the units of a_{XX} ($cm^2\ d^{-1}\ (°C)^{-1}$), kin_{anox} ($\mu mol\ NO_3\ L^{-1}$), Db_{coeff} (cm), PB (d^{-1}) and N:C ($mol\ N\ (mol\ C)^{-1}$).

Some of the optimized parameters reach the lower or upper edge of the allowed range. This is stated explicitly in the revised manuscript (P17L336-337). We also added a column to Table 2 indicating the range of values allowed for each parameter during the optimization to make clear for which parameters this happens.

Comment:
12. Table 3. Why are FNO3 and FNH4 so high in comparison with the other data?

Response:

NH_4 and NO_3 fluxes represent a more difficult problem for the optimization and therefore their cost is larger. This is stated as follows in the revised manuscript:

P16L320-322: "*NH_4 and NO_3 fluxes represent a more difficult problem for the optimization and therefore their cost is larger, especially at station Z03.*"

Note that, as per our response to Comment 10, all fluxes contribute about equally at the outset of the optimization.

Comment:

13. Page4-Line7: 'a proportion of the deposited nitrogen is lost as N2 gas'. If the denitrification would work like this, it would mean that the sediments would never be a sink of nitrogen, which is in contradiction with the previous sentence (P4-L6). 'A proportion of organic matter is mineralized with nitrate' is a correct description of denitrification.

Response:

We modified the sentence "*a proportion of the deposited nitrogen is lost as biologically unavailable N gas (N_2)*" to "*a proportion of the deposited organic matter is remineralized via denitrification which produces biologically unavailable N_2 gas*".

Comment:

14. P14-L14: what is RMSE ? How does this relate to the cost (equation 3)?

Response:

We use the root mean square error (rather than the cost) to show that even though the total cost improves, the agreement between observed and modeled NH_4^+ profiles gets worse when the profiles are not included in the cost calculation. To clarify this point we modified the paragraph as follows (P18L363-367): "*However, when NH_4 profiles are not included in the cost calculation there is a large deviation between observed and modeled sediment NH_4 concentrations (not included in the cost). The root mean square error for the sediment profiles increases from 87.59 mmol N m^{-2} d^{-1} for the baseline case to 174.45 mmol N m^{-2} d^{-1} (Site-specific, flux only) and 111.86 mmol N m^{-2} d^{-1} (Site-specific, flux only + FPOM).*"

Comment:

15. P20L22 What does the metamodel do when there is an O2-debt ? I assume this means that negative oxygen concentrations arise in the pelagic model – were negative oxygen concentrations used for fitting the metamodel?

Is the consumption of oxygen in the absence of a PON flux caused by the nitrification of ammonium that fluxes into the sediment or is it a statistical artifact (it appears to be quite high)?

Response:

For anoxic bottom waters, the O_2-debt is represented by negative O_2 concentrations in the biogeochemical models (see P28L576-579). We did not use negative O_2 concentrations to fit the meta-model. These waters are anoxic and we used $O_2 = 0$ in these cases.

The occurrence of nitrification in the sediment explains the O_2 consumption in the absence of PON flux. This is clearer in the revised Figure 7 (see Figure 2), which shows that O_2 and NH_4 uptake by the sediment occur at low PON flux in the meta-model.

References:

Chatterjee, S., Laudato, M. and Lynch, L. A.: Genetic algorithms and their statistical applications: an introduction, Comput. Stat. Data Anal., 22(6), 633–651, doi:10.1016/0167-9473(96)00011-4, 1996.

Fogel, D. B.: An introduction to simulated evolutionary optimization., IEEE Trans. neural networks, 5(1), 3–14, doi:10.1109/72.265956, 1994.

Friedrichs, M. A. M.: A data assimilative marine ecosystem model of the central equatorial Pacific: Numerical twin experiments, J. Mar. Res., 59(6), 859–894, doi:10.1357/00222400160497544, 2001.

Friedrichs, M. A. M., Dusenberry, J. A., Anderson, L. A., Armstrong, R. A., Chai, F., Christian, J. R., Doney, S. C., Dunne, J., Fujii, M., Hood, R., McGillicuddy, D. J., Moore, J. K., Schartau, M., Spitz, Y. H. and Wiggert, J. D.: Assessment of skill and portability in regional marine biogeochemical models: Role of multiple planktonic groups, J. Geophys. Res., 112(C8), C08001, doi:10.1029/2006JC003852, 2007.

Hibbert, D. B.: Genetic algorithms in chemistry, Chemom. Intell. Lab. Syst., 19(3), 277–293, doi:10.1016/0169-7439(93)80028-G, 1993.

Kane, A., Moulin, C., Thiria, S., Bopp, L., Berrada, M., Tagliabue, A., Crépon, M., Aumont, O. and Badran, F.: Improving the parameters of a global ocean biogeochemical model via variational assimilation of in situ data at five time series stations, J. Geophys. Res., 116(C6), C06011, doi:10.1029/2009JC006005, 2011.

Kolda, T. G., Lewis, R. M. and Torczon, V.: Optimization by direct search: New perspectives on some classical and modern methods, SIAM Rev., 45(3), 385–482, doi:Doi 10.1137/S003614450242889, 2003.

Kuhn, A. M., Fennel, K. and Mattern, J. P.: Model investigations of the North Atlantic spring bloom initiation, Prog. Oceanogr., doi:10.1016/j.pocean.2015.07.004, 2015.

Robson, B., Hamilton, D., Webster, I. and Chan, T.: Ten steps applied to development and evaluation of process-based biogeochemical models of estuaries, Environ. Model. Softw., 23(4), 369–384, doi:10.1016/j.envsoft.2007.05.019, 2008.

Schartau, M. and Oschlies, A.: Simultaneous data-based optimization of a 1D-ecosystem model at three locations in the North Atlantic: Part I—Method and parameter estimates, J. Mar. Res., 61(6), 765–793, doi:10.1357/002224003322981147, 2003.

Ward, B. a., Friedrichs, M. a. M., Anderson, T. R. and Oschlies, A.: Parameter optimisation techniques and the problem of underdetermination in marine biogeochemical models, J. Mar. Syst., 81(1-2), 34–43, doi:10.1016/j.jmarsys.2009.12.005, 2010.

Wilson, R. F., Fennel, K. and Paul Mattern, J.: Simulating sediment–water exchange of nutrients and oxygen: A comparative assessment of models against mesocosm observations, Cont. Shelf Res., 63, 69–84, doi:10.1016/j.csr.2013.05.003, 2013.

Wood, C. C., Statham, P. J., Kelly-Gerreyn, B. a. and Martin, A. P.: Modelling macronutrients in shelf sea sediments: fitting model output to experimental data using a genetic algorithm, J. Soils Sediments, 14(1), 218–229, doi:10.1007/s11368-013-0793-0, 2013.

Parameterization of biogeochemical sediment-water fluxes using in-situ measurements and a diagenetic model

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Abstract

Diagenetic processes are important drivers of water column biogeochemistry in coastal areas. For example, sediment oxygen consumption can be a significant contributor to oxygen depletion in hypoxic systems, and sediment-water nutrient fluxes support primary productivity in the overlying water column. Moreover, non-linearities develop between bottom water conditions and sediment-water fluxes due to loss of oxygen-dependent processes in the sediment as oxygen becomes depleted in bottom waters. Yet, sediment-water fluxes of chemical species are often parameterized crudely in coupled physical-biogeochemical models, using simple linear parameterizations that are only poorly constrained by observations. Diagenetic models that represent sediment biogeochemistry are available, but rarely are coupled to water column biogeochemical models because they are computationally expensive. Here, we apply a method that efficiently parameterizes sediment-water fluxes of oxygen, nitrate and ammonium by combining *in situ* measurements, a diagenetic model and a parameter optimization method. As a

proof of concept, we apply this method to the Louisiana Shelf where high primary production, stimulated by excessive nutrient loads from the Mississippi-Atchafalaya River system, promotes the development of hypoxic bottom waters in summer. The parameterized sediment-water fluxes represent non-linear feedbacks between water column and sediment processes at low bottom water oxygen concentrations, which may persist for long periods (weeks to months) in hypoxic systems such as the Louisiana Shelf. This method can be applied to other systems and is particularly relevant for shallow coastal and estuarine waters where the interaction between sediment and water column is strong and hypoxia is prone to occur due to land-based nutrient loads.

1. Introduction

Sediment biogeochemistry represents a major component of elemental cycling on continental margins (Middelburg & Soetaert, 2005; Liu et al., 2010). In these shallow, productive areas on average 30% of photosynthetically produced organic matter is deposited and recycled in the sediment (Wollast, 1998). The recycling of this organic material consumes oxygen (O_2) and can result in either a source or a sink of nutrients to the water column (Cowan and Boynton, 1996). For instance, a proportion of the deposited organic matter is remineralized via denitrification which produces biologically unavailable N_2 gas. Denitrification represents a major removal pathway for nitrogen (N) in coastal areas (Fennel et al., 2009, Bohlen et al., 2012) and buffers the effects of excessive N loads in eutrophic systems (Seitzinger & Nixon, 1985). In this type of environment, high respiration rates in the water column and in the sediment may lead to bottom O_2 depletion under stratified conditions, resulting in bottom water hypoxia ($O_2 < 62.5$ mmol O_2 m^{-3}) or anoxia (absence of O_2). Under low O_2 conditions, coupled nitrification-denitrification in the sediment is inhibited and remineralized N may return entirely to the water column as ammonium (NH_4^+), readily available to primary producers, which constitutes a positive feedback on eutrophication (Kemp et al., 1990). Conversely, N removal into N_2 may increase due to direct denitrification or due to anammox if a source of nitrate/nitrite is available (Neubacher et al., 2012). O_2-dependent sediment-water interactions are therefore particularly important in low O_2 environments.

Clearly, the strong benthic-pelagic interaction is a key aspect of coastal biogeochemistry that needs to be represented accurately in biogeochemical models. However, sediment-water fluxes in models are often difficult to parameterize, being poorly constrained by observations. One of the simplest approaches to parameterizing sediment-water fluxes is using a reflective boundary where fluxes are proportional to particulate organic matter (POM) deposition (e.g. Fennel et al., 2006). Empirical relationships can be used to represent sediment biogeochemical processes, such as denitrification (Fennel et al., 2009) or sediment O_2 consumption (SOC) (Hetland and DiMarco, 2008). An advantage of these first-order sediment-water flux parameterizations is that they are computationally extremely efficient and can be sufficient depending on the type of environment and the focus of the study (Wilson et al., 2013). However, sediment-water flux parameterizations are a coarse representation of sediment-water interaction and typically do not capture non-linearities in nutrient fluxes which occur under hypoxic/anoxic conditions. Moreover, the choice of parameterization can have a significant effect on model results as shown in Fennel et al. (2013) where different parameterizations of SOC led to dramatically different regions of hypoxia.

Mechanistic models of diagenesis are more realistic representations of sediment biogeochemistry (Rabouille & Gaillard, 1991; Soetaert & Herman, 1995; Soetaert et al., 1996a; DiToro, 2001, Meysman et al., 2003a,b). They are forced by POM deposition and bottom water conditions, and simulate aerobic and anaerobic remineralization pathways including processes such as nitrification, denitrification, the anaerobic production of reduced substances—represented either explicitly or lumped together in O_2 demand units (ODU)—and the resulting flux of O_2 and nutrients across the sediment-water interface. While these models have been useful for studies of sediment biogeochemistry (Middelburg et al., 1996; Soetaert et al., 1996b; Boudreau et al, 1998; Meysman et al., 2003b) and for improving our understanding of sediment-water interactions (Katsev et al, 2007; Reed et al, 2011), their coupling to water column processes in biogeochemical circulation models is often limited or done at the expense of spatial resolution (Eldridge and Roelke, 2010) because of the increased computational cost. Furthermore, the diagenetic model parameter sets are often poorly constrained by observations and therefore these models do not necessarily perform better than the simple parameterizations (Wilson et al., 2013).

An alternative, computationally more efficient approach is to parameterize sediment-water fluxes from a diagenetic model using a meta-model of diagenetic processes, as recommended by Soetaert et al. (2000). Their mass conservative method is more realistic than the simple reflective boundary and computationally more efficient than a mechanistic model of diagenesis. The method requires addition of a vertically integrated pool of sedimentary particulate organic matter for each horizontal grid cell thus enabling a mass balanced approach, but adding a layer of complexity to the water column model. Here we further simplify the meta-modeling method of Soetaert et al (2000) by direct meta-modeling of sediment-water fluxes. Our method parameterizes sediment-water fluxes of O_2, $NO_3^-$and NH_4^+ in a coupled biogeochemical circulation model using in-situ measurements, a mechanistic model of early diagenesis and a parameter optimization technique. The method is universal but its application is region-specific due to the local characteristics of the sediment, e.g. sediment quality (POM concentration and lability), type (porosity) and species composition (bioturbation) that influence local sediment biogeochemistry and sediment-water fluxes and are reflected in the choice of diagenetic model parameters. We apply this method to the Louisiana Shelf in the northern Gulf of Mexico, where hypoxia develops annually due to eutrophication (Rabalais et al., 2002).

First, we calibrate the diagenetic model with the help of a genetic optimization algorithm using a set of observations collected on the Louisiana Shelf. We then implement the calibrated model to simulate time-resolved sediment biogeochemistry in the region and use the model results to compute a meta-model parameterization of sediment-water fluxes for O_2, NH_4^+ and NO_3^-. Finally, we compare the fluxes parameterized with the meta-model with previous relationships used for the Louisiana Shelf.

2. Materials and methods

2.1. Observations

The data used for optimization of the diagenetic model parameters were collected at two locations along the 20 m isobath on the Louisiana Shelf (Figure 1) during 3 cruises in April, June and September 2006 (Murrell et al., 2013). The two locations experience hypoxia in summer but have distinct hydrographic and biological regimes. Station Z02 (see Murrell et al., 2013, for details on sampling design) is located off Terrebonne Bay on the eastern Louisiana Shelf and is influenced by river discharges from the Mississippi Delta with high primary productivity and high POM depositional flux. Station Z03 is located southwest of Atchafalaya Bay on the western Louisiana Shelf with somewhat higher salinity and lower chlorophyll concentrations than station Z02 (Lehrter et al., 2009; 2012). The dataset includes bottom water properties (temperature, salinity, O_2 and nutrients, Table 1), sediment-water fluxes (O_2, nutrients) and NH_4^+ sediment profiles (Figure 2). On each date, eight sediment cores were collected at each station (3 for O_2 flux, 3 for nutrient fluxes and 2 for sediment profiles). O_2 and nutrient fluxes were measured on site from triplicate individual incubations in sediment chambers. Sediment NH_4^+ concentration was measured for each 2 cm bin in the duplicate sediment cores. Bottom water temperature and salinity were measured with a CTD, whereas O_2 and nutrient concentrations were measured in the water overlying the sediment cores. Details on the dataset are available in Lehrter et al. (2012), Murrell et al. (2013) and Devereux et al. (2015).

2.2. Sediment flux parameterization

The parameterization of sediment-water fluxes was derived using output from a diagenetic model. The diagenetic model was first optimized using the observational dataset described in the previous section. The optimized diagenetic model was then run multiple times to derive meta-model parameterizations.

2.2.1. Diagenetic model

The diagenetic model represents the dynamics of the key constituents of the sediment (solids and pore water) involved in early diagenesis, as formulated by Soetaert et al. (1996a,b). The model is vertically resolved, and represents the upper 10 cm of the sediment using 10 layers with increasing resolution toward the surface. The diagenetic model has 6 state variables: the solid volume of organic carbon (OC), which is split into a labile class (which remineralizes rapidly) and a refractory class (which remineralizes slowly), NH_4^+, NO_3^-, O_2 and ODU. Reduced substances produced by anoxic remineralization are added to the ODU pool rather than being explicitly modeled. Model processes include aerobic remineralization, nitrification, denitrification, anaerobic remineralization and ODU oxidation. Dissimilatory nitrate reduction to ammonium (DNRA) and anaerobic ammonium oxidation (anammox) are not explicitly represented in the model. Vertical transport of solid and pore water constituents depend on sedimentation of POM to the sediment, and on diffusion, bioturbation and permanent burial. The burial of ODU refers to the deposition of ODUs as solids (e.g., pyrite, manganese carbonate) below the bioturbated zone (Soetaert et al., 1996a). The model simulates sediment-water fluxes of pore water constituents, namely NH_4^+, NO_3^-, O_2 and ODU. We assume that ODUs are oxidized instantaneously in the water column when O_2 is available. Therefore, the net O_2 flux into the sediment is the addition of the direct O_2 flux necessary for nitrification, oxidation of ODUs and of POM in the sediment, termed SOC, plus the O_2 sink in bottom waters necessary to oxidize any ODU efflux from the sediment.

The original model of Soetaert et al. (1996a,b) was modified as follows. A temperature-dependency was introduced for the remineralization of the two organic matter pools and the bioturbation of solids following a Q_{10} relationship such that:

$$R_i(T) = R_i^{T_b} \times \theta^{(T-T_b)/10} \tag{1}$$

where $R_i(T)$ and $R_i^{T_b}$ (y^{-1}) are the remineralization or bioturbation at ambient temperature (T; °C) and at the base temperature (T_b; °C) (i.e., $R_1^{T_b}$ and $R_2^{T_b}$ for remineralization and $Dbio_0$ for bioturbation, Table 2) and θ is the Q_{10} factor. In the updated model temperature thus influences the solute diffusivity, the degradability of the two OM pools and bioturbation. This modification allows for the representation of temperature-dependence of microbial processes in the sediment (aerobic respiration, denitrification and anaerobic metabolism), which is known to be important in coastal systems (see, e.g., Fig. 5 in Wilson et al. 2013). Nitrification is not temperature dependent in the diagenetic model. It is assumed that O_2 concentration is the main factor limiting nitrification in the Louisiana Shelf sediments.

Non-local mixing of pore water constituents due to bioturbation (irrigation) was also introduced and formulated following Boudreau (1997) such that:

$$I(z) = \alpha(z) \cdot (C_{ow} - C(z)) \tag{2}$$

where $I(z)$ (μmol L^{-1} y^{-1}) is the irrigation at depth z, C_{ow} and $C(z)$ (μmol L^{-1}) are the solute concentration at the sediment-water interface and at depth z in the sediment, respectively. $\alpha(z)$ is the rate of non-local exchanges at depth z such that $\alpha(z) = \alpha_0 \cdot f(z)$, where α_0 (y^{-1}) is the rate at $z = 0$ and $f(z)$ is a function representing the decay of α with depth. Here, $f(z)$ is the same function as for the bioturbation of solids (Soetaert et al., 1996a). Bioturbation and non-local mixing of solutes are not dependent on O_2 in the model. Such a dependence could be introduced to account for repeated cycles of eradication/re-establishment of macrofauna due to anoxia. However, given the limited information on the relationship between porewater O_2, infauna biomass and irrigation in this region (Eldridge and Morse, 2008), we assumed that macrobiota does not re-establish itself in the regions affected by recurring severe seasonal hypoxia or anoxia on the Louisiana Shelf and thus do not expect a strong dependence of bioturbation and bioirrigation on O_2.

The model has a total of 36 parameters (Table 2). Sediment porosity parameters were chosen to obtain a porosity profile that is within the range observed on the Louisiana Shelf. Given a lack of observations, the nitrogen to carbon ratio (N:C; mol N (mol C)$^{-1}$) of the labile and refractory fraction of OC were fixed to constant values following Wilson et al. (2013). The assumption is that N:C follows Redfield (Redfield et al., 1963) in the labile fraction (N:C = 0.15), whereas the proportion of carbon increases in the refractory fraction (N:C = 0.10). Since deposited OC mainly originates from local primary production on the shallow Louisiana Shelf (Redalje et al., 1994; Justić et al., 1996; Rowe and Chapman, 2002), labile OC is assumed to represent 74% of total OC in deposited material. This value was used by Soetaert et al. (1996a) to represent the fraction of labile organic matter in surface waters and is in line with previous modeling investigations of the Louisiana Shelf (Justić et al., 1996; Eldridge and Morse, 2008). However, inshore areas adjacent to river discharge may have higher fraction of terrestrial organic matter. The exponential decay coefficient for bioturbation was set as in the original model (Soetaert et al., 1996a).

Solute-specific diffusion coefficients (D_i^T; cm^2 d^{-1}) at ambient temperature *T* were calculated following Soetaert et al. (1996a) and Li & Gregory (1974) such that $D_i^T = D_i + \alpha_i T$, where D_i (cm^2 d^{-1}) is the solute-specific diffusion coefficient at 0°C and α_i (cm^2 d^{-1} (°C)$^{-1}$) is the solute-specific temperature dependency coefficient (Table 2). The 20 remaining parameters of the diagenetic model (Table 2) were optimized to obtain the best match between the observed and simulated sediment profiles and sediment-water fluxes.

2.2.2. Parameter optimization

The diagenetic model parameters were first optimized to match the sediment-water fluxes and sediment NH_4^+ concentrations observed in April, June and September 2006 at station Z02 and Z03. The sampling frequency at these stations did not allow construction of a reasonable time-dependent forcing dataset for the diagenetic model (i.e. solute concentrations in overlying water, POM deposition). Thus, we didn't run the optimization in a time-dependent mode; instead the model was run for 300 days with constant forcing for each time and location where observations were available. During the optimization the model was forced with observed bottom water conditions, namely salinity, temperature, NH_4^+, NO_3^-, and O_2 (Table 1). Since no observations of POM depositional flux were available, POM depositional fluxes were prescribed using monthly means calculated for station Z02 and Z03 from a multiyear biogeochemical model simulation (see Section 2.2.3). The mean depositional fluxes do not represent short-lived deposition events which is appropriate for a model with constant forcing.

Optimization of the parameter set was carried out with the help of an evolutionary algorithm. This stochastic technique mimics natural selection by iteratively selecting the “fittest” set of parameters to reproduce the observations. The evolutionary algorithm is a well accepted method for optimization problems (Hibbert, 1993; Fogel, 1994; Chatterjee et al., 1996; Kolda et al., 2003) and has been increasingly used to optimize parameters in biogeochemical models (Kuhn et al., 2015; Robson et al., 2008; Schartau and Oschlies, 2003; Ward et al., 2010). The technique was successfully used for the optimization of parameters of Soetaert et al.’s (1996a) diagenetic model in two independent studies (Wilson et al., 2013; Wood et al., 2013). The advantage of the evolutionary algorithm over traditionally used gradient-descent algorithms is that it explores the parameter space with an element of randomness and therefore is less prone to converging on a local minimum. Each parameter is given a range of variation within which the algorithm will search for the best value to match the observations. Regardless of which minimization technique is used, gradient-descent or an evolutionary algorithm, some parameters may not be identifiable because they are unconstrained by the available observations (Soetaert et al., 1998; Fennel et al., 2001).

The evolutionary algorithm works as follows. Each set of parameters is considered to be a single individual. An initial set of *n* individuals includes the initial parameter set and $n-1$ individuals generated randomly from this initial set of parameters through the addition of log-normally distributed random noise. The diagenetic model is run with the *n* parameter sets, and the difference between the results and observations is quantified using a cost function, which measures the misfit between the observations and their model counterparts. The fittest $\mathrm{n}/2$ individuals, i.e. those with the lowest cost, become the parent population and a next generation of $\mathrm{n}/2$ individuals (child population) is created by recombination of the parameters from the fitter half of the population and by mutation, which occurs through the addition of random noise. The model is run again for all the parameter sets of the child population, and the above procedure repeated for *k* generations. The fittest individual after *k* generations is the optimized parameter set. Here, we used $\mathrm{n} = 30$ population members and $\mathrm{k} = 200$ generations. The chosen value of *k* is large enough to allow the results to converge.

Ideally a single parameter set should capture the temporal and spatial variability of sediment processes throughout the Louisiana Shelf. For this reason, the diagenetic model was run with identical parameters in all 6 model configurations (3 dates, 2 locations), each corresponding to a set of observed bottom water conditions plus estimated F_{POM} (Table 1). Model results were compared with their corresponding set of sediment observations (NH_4^+ porewater concentrations and sediment-water fluxes) using a cost function that includes all model variables at the 6 locations/times. The smaller the cost, the fitter is an individual (i.e. parameter set) during the evolutionary optimization process. The cost function F for the parameter set $\vec{p}$ was calculated as follows:

$$F(\boldsymbol{p}) = \sum_{s=1}^{l}\sum_{t=1}^{m}\left(\sum_{i=1}^{n}\left(\frac{1}{w_i} \times \frac{(X_{s,t,i}^{mod}(\vec{p}) - X_{s,t,i}^{obs})^2}{\sigma_{s,t,i}^2}\right)\right) \tag{3}$$

where *s* refers to locations Z02 and Z03, *t* is the sampling date (3 in 2006) and *i* is the observation type: 3 sediment-water fluxes (SOC, NH_4^+ and NO_3^-) and 1 sediment profile (NH_4^+). X^{obs} and X^{mod} represent the observed and simulated variable, respectively; $\sigma_{s,t,i}^2$ is the observation standard deviation; and $1/w_i$ represents the weight of each variable in the cost function. The values of w_i were calculated for each variable *i* as the cost of a diagenetic model run using the initial parameter set $\boldsymbol{p_0}$ such that $w_i = F_i(\boldsymbol{p_0})$. The weight gives the variables approximately equal influence on the overall cost, at least initially. The weighting approach is common in parameter optimization studies (see, e.g., Friedrichs, 2001; Schartau and Oschlies, 2003; Friedrichs et al., 2007; Kane et al., 2011). To avoid biasing the cost calculation toward the NH_4^+ profiles we computed an average cost per profile.

The sensitivity of the optimized model to parameter changes was assessed by successively varying each parameter by ±50% and calculating the change in the total cost. Then the influence of observations and forcing datasets on the optimization results was assessed as follows. First, the optimization was carried out for each station individually (to obtain site-specific parameters); then sediment profiles were excluded from the optimization (to obtain site-specific parameters optimized for flux data only) and, finally, POM depositional fluxes were included as additional parameters in the optimization rather than prescribed (to obtain site-specific parameters and F_{POM} optimized for flux data only).

2.2.3. Meta-modeling procedure

Our meta-modeling procedure parameterizes sediment-water fluxes by means of a multivariate regression model that relates bottom water conditions and depositional flux to sediment-water fluxes, and was used here to parameterize Louisiana Shelf fluxes at the sediment-water interface. Using a meta-model of sediment-water fluxes is a simplification of the method proposed by Soetaert et al. (2000) who used a meta-model of diagenetic processes (rates) instead. The aim of our technique is to combine the simplicity and efficiency of a sediment-water flux parameterization with the realism of a diagenetic model. It is important to note that our simplified meta-model is not mass conservative; however, as long as the method is used for the system for which it was developed and within the range of conditions that were used for the parameterization, violation of mass conservation should be minor. An advantage of our simplification is that it does not require knowledge of integrated POM concentration in the sediment.

In order to obtain the meta-model parameterization the diagenetic model was run many times in time-varying mode using the single parameter set optimized for the Louisiana Shelf. The diagenetic model was forced with multi-year time series of bottom water conditions obtained from a biogeochemical circulation model of the Louisiana Shelf based on the Regional Ocean Modeling System (ROMS; Figure 3). The simulation is described in Fennel et al. (2013) (case B20clim) and covers the period from 2004 to 2009. The same simulation was used to prescribe POM depositional fluxes during the parameter optimization. For details on the model set up and validation we refer the reader to Fennel et al. (2013). We included only those grid cells on the Louisiana Shelf ($z < 50$ m) and west of the Mississippi River delta. Each grid cell (3791 in total) provides a time series of bottom water temperature, salinity, NO_3^-, NH_4^+, O_2 and POM depositional flux conditions that was used to run the optimized diagenetic model. We consider

2004 as a spin up year for the diagenetic model and selected the period 2005-2009 for analysis. Half of the data from each simulation were randomly chosen to derive the meta-model. The multivariate meta-model regressions were then calculated to relate bottom water conditions and depositional flux (model inputs) to the corresponding sediment-water fluxes (model output) using the $3.45 \cdot 10^6$ data vectors. To validate the meta-model we calculated correlation coefficients between the remaining data of each diagenetic model simulation (i.e. at each model grid location) and the corresponding meta-model results.

Each regression model is expressed as follows:

$$y = a + \sum_{i=1}^{n} (b_i x_i + c_i x_i^2 + d_i x_i^3) \qquad (4)$$

where each x_i corresponds to an explanatory variable i, and a, b_i, c_i and d_i are the coefficients for the zero-order term, the regular term (x_i), the squared term (x_i^2) and the cubic term (x_i^3), respectively.

2.3. Other flux parameterizations

The meta-model parameterizations are compared with three other sediment-water flux parameterizations that have been used previously in our biogeochemical circulation model for the northern Gulf of Mexico (reviewed by Fennel et al., 2013). All three parameterizations represent SOC and NH_4^+ flux only. The first (Eq. 5-6), referred to as IR, assumes instantaneous remineralization of deposited PON into NH_4^+ while a fraction of N is lost through denitrification. IR is formulated as follows (Fennel et al., 2006; 2009):

$$F_{\mathrm{NH_4^+}}^{IR} = r_{\mathrm{NH_4^+}} \cdot (w_P Phy + w_S SDet + w_L LDet), \tag{5}$$

$$F_{\mathrm{O_2}}^{IR} = -r_{O_2:\mathrm{NH_4^+}} F_{\mathrm{NH_4^+}}^{IR}, \tag{6}$$

with $r_{\mathrm{NH_4^+}} = 4/16$ mmol $\mathrm{NH_4^+}$ per mol PON and $r_{O_2:N} = 115/16$ mmol $\mathrm{O_2}$ per mol $\mathrm{NH_4^+}$. w_P, w_S and w_L are the sinking rate of phytoplankton (Phy) and small (SDet) and large (LDet) detritus, respectively.

The other two parameterizations assume that SOC depends on bottom water $\mathrm{O_2}$ and temperature (T) only and ignore POM deposition. One, referred to as H&D (Eq. 7), is from Hetland & DiMarco (2008). The other, referred to as M&L (Eq. 8), is from Murrell & Lehrter (2011) with a temperature-dependence added by Fennel et al. (2013). Sediment-water $\mathrm{O_2}$ fluxes are formulated as follows:

$$F_{\mathrm{O_2}}^{H\&D} = 6 \cdot 2^{T/10} \cdot \left(1 - e^{-O_2/30}\right), \tag{7}$$

$$F_{\mathrm{O_2}}^{M\&L} = 0.0235 \cdot 2^{T/10} \cdot O_2, \tag{8}$$

For each parameterization x the sediment-water $\mathrm{NH_4^+}$ flux is a function of SOC such that:

$$F_{\mathrm{NH_4^+}}^{x} = -r_{\mathrm{NH_4^+}:SOC} F_{\mathrm{O_2}}^{x}, \tag{9}$$

with $r_{\mathrm{NH_4^+}:SOC} = 0.036$ mmol $\mathrm{NH_4^+}$ per mmol $\mathrm{O_2}$.

3. Results

3.1. Diagenetic model parameter optimization

Optimization of the diagenetic model parameters lowered the cost function (Eq. 3) significantly compared to the original parameter set (Table 3). NH_4^+ profiles and sediment-water fluxes simulated with the optimized parameters are, in most cases, within two standard deviations of the observations (Figure 2). Simulated O_2 fluxes match the observations at station Z02 but are underestimated somewhat in April and June at station Z03. Observed O_2 fluxes are relatively high in April and June at station Z03 despite low sediment-water nutrient fluxes and NH_4^+ concentration in the sediment. Observed O_2 flux had a very large standard deviation in April at station Z03 and therefore did not influence the optimization. NH_4^+ and NO_3^- fluxes represent a more difficult problem for the optimization and therefore their cost is larger, especially at station Z03. Overall, sediment-water fluxes are better simulated at station Z02 and therefore station Z03 contributes more the total cost for the optimized parameter set (Table 3). Temporal variations in NH_4^+ and NO_3^- fluxes are in qualitative agreement with observations although the model underestimates their magnitudes (Figure 2). The model is able to simulate observed NO_3^- flux realistically, in particular the observed NO_3^- flux into the sediment under low bottom O_2 conditions (Figure 2). Within the sediment, simulated NH_4^+ concentrations agree with observations in April and June, but are underestimated in September. High NH_4^+ concentrations were observed at station Z02 at this time despite low NH_4^+ effluxes from the sediment. Note that the observations have large standard deviations for this case and therefore this NH_4^+ sediment profile had only a small influence on the optimization. Some of the observed NH_4^+ profiles in April and September display a gradient at depth (Figure 2) that the diagenetic model might not be able to resolve. There is also a deep negative gradient in the simulated profiles in April indicating that the model didn't reach full steady state conditions at depth. However, this mismatch at depth has a limited effect on sediment-water fluxes.

Within the optimized parameter set, several parameter values reached the lower or upper edge of their allowed range, which can be informative about the dynamics of the system (Table 2). Except for the bioturbation diffusivity ($Dbio_0$), all other parameters associated with bioturbation reduced the effect of bioturbation on sediment-water fluxes over the course of the optimization: the depth of the bioturbated layer (z_{bio}) decreased to 1 cm; the optimized Q_{10} factor for bioturbation (θ_{bio}) moved to the lower limit of the Q_{10} range ($2 < \theta < 3$); and the non-local mixing coefficient (α_0) was reduced to a small value essentially removing the influence of non-local mixing from the system. In addition to the reduction in bioturbation, permanent burial of ODUs does not occur in the optimized model (PB = 0, Table 2). Conversely, the optimized Q_{10} factors for the remineralization of the slow (θ_{r1}) and fast (θ_{r2}) decaying pools of organic matter are at their upper limits indicating a strong dependence of remineralization on temperature (Table 2). For denitrification, the optimized value for the inhibition effect of NO_3^- (k_{dnf}) is low compared to the original parameter, whereas the inhibition effect of O_2 (kin_{dnf}) is high (Table 2). The inhibition effect of O_2 on nitrification (k_{nit}) and of NO_3^- (kin_{anox}) and O_2 (kin_{odu}) on anaerobic remineralization is small in comparison to the original parameters. The maximum rate of nitrification (Nit) is significantly higher than in the original parameter set (Table 2).

We examined the sources of model-data discrepancies by sequentially releasing part of the constraints on the parameter optimization (Figure 2, Table 3). Optimizing station Z02 and Z03 separately improves the total cost by decreasing the cost associated with NH_4^+ and NO_3^-

fluxes (Table 3), in particular for NO_3^- at station Z02 (Figure 3, Table 3). Removing the constraint of sediment NH_4^+ profiles from the optimization improves the total cost further (Table 3). This is due, in part, to the absence of NH_4^+ profiles from the cost calculation, but also to somewhat improved sediment-water fluxes (Figure 2). The best agreement between simulated and observed sediment-water fluxes is achieved by including POM depositional fluxes as additional parameter to optimize (Figure 3, Table 3). In this case POM deposition is increased in June (×2 and ×1.3 at station Z02 and Z03, respectively) and reduced in spring (×0.5 and ×0.25 at station Z02 and Z03, respectively) and fall (×0.5 at station Z03) and the cost associated with NO_3^- and NH_4^+ fluxes decreases significantly (Table 3). However, when NH_4^+ profiles are not included in the cost calculation there is a large deviation between observed and modeled sediment NH_4^+ concentrations (not included in the cost). The root mean square error for the sediment profiles increases from 87.59 mmol N m^{-2} d^{-1} for the baseline case to 174.45 mmol N m^{-2} d^{-1} (*Site-specific, flux only*) and 111.86 mmol N m^{-2} d^{-1} (*Site-specific, flux only* + F_{POM}). Since the parameter set with all constraints best represents sediment-water fluxes and NH_4^+ sediment concentrations throughout the Louisiana Shelf, it is used subsequently to parameterize sediment-water fluxes and is referred to as baseline.

For most of the parameter set, the optimized model is insensitive to parameter variation (Figure 5). The most sensitive process in the diagenetic model is the remineralization of the fast decaying organic matter pool, since the optimized model is sensitive to all the associated parameters, namely the remineralization of the fast decaying organic matter pool ($R_2(T)$), the base temperature (T_b) and the Q_{10} factor for fast decaying organic matter (θ_{r1}) in the Q_{10} relationship. The optimized model is also sensitive to the variation in POM deposition rates at station Z03 ($F_{POM}3_x$), mainly in June. Variation in deposition rates at station Z02, however, does not influence the overall cost. The sensitivity to parameters or model forcing related to organic matter is not surprizing given the high magnitude and large temporal and spatial variations in POM deposition in this region. Nonetheless, it highlights the overall uncertainty in the optimized model due to the lack of observations on depositional flux. The difference in sensitivities to the depositional flux at stations Z02 and Z03 can be explained by the magnitude of the total cost, which is higher at station Z03 (Table 3). The cost at station Z02 is sensitive to the POM deposition rate (e.g. >300% increase in April), but since the cost at station Z03 is much higher, the effect on the total cost is small. The uncertainty associated with POM deposition rates is then larger at station Z03. To a lesser extent, the optimized model is sensitive to the bioturbation diffusivity (D_{bio_0}) and to the maximum rate of nitrification (Nit). The cost is largest for NO_3^- flux (Table 3), which indicates that the optimization has more difficulty fitting the observations for this flux. The sensitivity of the optimized value for nitrification rate, which influence NO_3^- flux, is therefore higher.

3.2. Meta-modeling parameterization

A meta-model of sediment-water fluxes was derived using simulations with the optimized diagenetic model, as described in section 2.2.3. The coefficients of the meta-model parameterizations for O_2, NH_4^+ and NO_3^- sediment-water fluxes and the range of bottom water conditions used for the parameterization are presented in Table 4. Each parameterization is able to reproduce the sediment-water fluxes simulated with the diagenetic model (Figure 6). The spatially resolved correlation coefficients are above 0.8 for most of the Louisiana Shelf for O_2 and NH_4^+ fluxes and above 0.6 for NO_3^- fluxes (Figure 6). The parameterization fails to retrieve the simulated fluxes in some limited areas near the offshore limit of the shelf. Bottom water conditions for depths greater than 50 m were not included in the meta-modeling parameterization, which explains why the meta-model does not perform well at a few limited areas along the 50 m isobath.

Overall, the main contributors to the meta-model are temperature, salinity and O_2 (Table 4). The average contribution of POM deposition is low (Table 4, Figure 7). The time dependency between POM deposition and sediment-water fluxes is implicit in the meta-model and therefore instant POM deposition is not a good predictor of sediment-water fluxes. Temperature is the largest contributor for all fluxes (Table 4) and is associated with the seasonal variation in sediment-water fluxes. Salinity is not included in the diagenetic model but is a significant contributor in the meta-model because it is associated with the spatial variation in sediment-water fluxes on the Louisiana Shelf. Bottom water O_2 has a growing effect on NH_4^+ and NO_3^- flux under hypoxic conditions (Table 4, Figure 6). When bottom water O_2 is low, NH_4^+ flux increases with decreasing O_2. More deposited particulate organic N is thus returned to the water column as NH_4^+. O_2 concentration controls both the direction and intensity of NO_3^- flux in the meta-model. With oxygenated bottom waters, NO_3^- flux depends on bottom NO_3^- concentration due to NO_3^- diffusion across the sediment-water interface. NO_3^- flux is into the sediment when the bottom water NO_3^- concentration is high and out of the sediment when the bottom water NO_3^- concentration is low. When bottom waters are hypoxic, NO_3^- flux is oriented into the sediment, which then becomes a sink for water column NO_3^- (Figure 7).

By using simulated bottom water conditions from our biogeochemical circulation model as input for the meta-model we can assess the spatial and temporal variability in parameterized sediment-water fluxes over the Louisiana Shelf (see Figure 8 and 9). Sediment-water fluxes were computed from the meta-model in mid August 2009 (Figure 8) and throughout 2009 at station Z02 and Z03 (Figure 9). Bottom water conditions are presented in Figure 3. The spatial distribution of parameterized O_2 and NH_4^+ fluxes are somewhat similar (Figure 8), with large fluxes near Atchafalaya Bay and the Mississippi River delta where POM deposition is high in late Spring (> 5 mmol N m^{-2} d^{-1}, Figure 3). Patches of moderate to high NH_4^+ flux (1–4 mmol N m^{-2} d^{-1}) occur southwest of Terrebonne Bay and further west on the shelf where bottom waters are hypoxic (Figure 8). NO_3^- flux follows the distribution of bottom water O_2 on the shelf with flux into the sediment in hypoxic areas and flux out of the sediment elsewhere (Figure 8).

The time series at stations Z02 and Z03 indicate high temporal variability in parameterized sediment-water fluxes in summer (Figure 9) that are driven by rapid changes in bottom water conditions (Figure 3). The difference in the magnitude of O_2 flux is large between the two stations and coincides with the distinct POM deposition rate at the two stations in spring and early summer (Figure 9). This time-dependent effect is implicit in the meta-model. A similar pattern occurs for NH_4^+ flux at station Z02 (Figure 9). The annual peak in NH_4^+ flux occurs under hypoxic conditions. In late summer and fall, transient hypoxic conditions at station Z03 result in enhanced NH_4^+ flux to the water column. The direction and magnitude of NO_3^- fluxes closely follows the O_2 concentration in bottom water. Hypoxic conditions starting in early July at station Z02 result in a switch from efflux of NO_3^- from the sediment to influx of NO_3^- into the sediment

(Figure 9). As for NH_4^+, rapid reversal in NO_3^- flux direction in late summer and fall at station Z03 is associated with changes between oxic and hypoxic conditions.

3.3. Comparison with other parameterizations

Here we explore the differences between the meta-models and the three sediment-water flux parameterizations we used previously in our ROMS models for the Louisiana Shelf, i.e. IR, which assumes instant remineralization of deposited POM, and H&D and M&L, which are functions of bottom temperature and O_2 concentration only. In contrast to the H&D and M&L parameterizations, O_2 flux has a relatively weak sensitivity to bottom water O_2 concentrations in the meta-model (Figure 10). O_2 flux decreases at low bottom water O_2 concentration but does not stop in anoxic conditions, as it is the case for H&D and M&L. In the model, at low O_2, ODUs become the dominant O_2 sink (due to ODU oxidation in the water column) and therefore the O_2 sink can be significant despite the lack of O_2 in bottom waters. Similar to the IR parameterization, O_2 flux increases with PON depositional flux, but this effect is much weaker in the meta-model (Figure 10).

The NH_4^+ flux parameterized with the meta-model falls within the range of the H&D and M&L parameterizations when O_2 is available (O_2 > 50 mmol O_2 m^{-3}, Figure 11). However, the meta-model differs significantly from H&D and M&L in hypoxic conditions; NH_4^+ flux increases with decreasing O_2, opposite to the H&D and M&L parameterizations. As for O_2 flux, the increase in NH_4^+ flux with PON deposition is weaker than in the IR parameterization (Figure 11). In the meta-model, the NH_4^+ flux is larger than in IR under hypoxic conditions and low PON deposition, and lower than in IR at high deposition.

Sediment-water fluxes were calculated by applying the meta-models to output from the biogeochemical circulation model and are compared to those parameterized with the H&D parameterization (Figure 12). O_2 fluxes are larger in the meta-model in the areas of hypoxia near the Mississippi and Atchafalaya river mouths and on the mid shelf (see Figure 7). O_2 fluxes are smaller in the meta-model in other regions, especially on the western Louisiana Shelf where bottom water salinity and O_2 concentrations are elevated. NH_4^+ flux is also much higher in the meta-model in regions where hypoxia occurs (Figure 12). In the other areas NH_4^+ flux is slightly lower in the meta-model.

4. Discussion

The meta-model procedure for parameterizing sediment-water fluxes requires a diagenetic model that realistically represents sediment processes. In order to obtain such a realistic diagenetic model for the Louisiana Shelf we optimized a modified version of Soetaert et al.'s model (1996a), which captures the main temporal variations in sediment biogeochemistry, sediment NH_4^+ concentration and sediment-water fluxes at the two sampling locations on the eastern and western Louisiana Shelf. An issue with the optimization of large parameter sets in diagenetic models is the poor identifiability of some parameters that results in a large uncertainty in their value (Soetaert et al., 1998). This caveat in our optimization approach would not be alleviated by using a different type of optimization. Several methods have been proposed to estimate parameter identifiability and uncertainty (Soetaert et al., 1998; Soetaert and Petzoldt, 2010, Fennel et al. 2001). However, a more complete set of observations would be necessary. The available observations were also not sufficient to allow running the diagenetic model in a time-dependent mode and therefore the optimization was carried out with constant forcing conditions. To evaluate the effect of parameter variations (i.e. uncertainty) on the model results we carried out a sensitivity analysis on the optimized model. A key driver of diagenetic processes is POM deposition and the remineralization of the labile deposited POM is the most sensitive parameter in the model. Observations of POM deposition were not available and using average rates of POM deposition from a biogeochemical model, as we have done here, is an additional source of uncertainty. This is demonstrated by the improved agreement between simulated and observed sediment-water fluxes when including POM deposition in the optimization.

Some of the discrepancies between model and observations can also be attributed to the imposition of a single parameter set. For example, sediment porosity and bioturbation are interdependent (Mulsow et al., 1998) and influence sediment-water fluxes (Aller, 1982). They are known to vary spatially on the Louisiana Shelf (Lehrter et al., 2012; Briggs et al., 2014), which is not represented in the optimized parameter set. This limitation could be resolved by introducing spatially dependent bioturbation and porosity coefficients; however, a much larger spatially resolved dataset would be necessary to obtain these dependencies. Another limitation is the observed deep gradient in some of the NH_4^+ profiles (e.g. in April), whereas the diagenetic model imposes a no gradient boundary condition a depth. Some mismatch between model and observations may also be generated by missing processes in the diagenetic model. As in earlier studies of the Louisiana Shelf (Morse and Eldridge, 2007; Eldridge and Morse, 2008), the diagenetic model does not represent DNRA and anammox. Although DNRA can be an important contributor to the N cycle under severe hypoxia (Dale et al., 2013), there is a poor understanding of the importance of DNRA on the Louisiana Shelf due to the lack of observations (Dagg et al., 2007). High porewater sulphide concentrations near the sediment-water interface are not reported for sediments of the Louisiana Shelf (Lin and Morse, 1991; Morse and Eldridge, 2007), which tend to minimize the importance of DNRA. However, the large NH_4^+ porewater concentrations observed at station Z02 in September (Figure 2) could be explained by the occurrence of DNRA. Anammox may also be a sink for bottom water NH_4^+ on the Louisiana Shelf (Lin et al., 2011). McCarthy et al. (2015) found that anammox may represent, at times, up to 30% of denitrification (including anammox) in some locations of the Louisiana Shelf. As a result, NH_4^+ flux to the water column may be overestimated by the diagenetic model, and in the parameterization, under low bottom O_2 conditions.

Overall, despite some discrepancies with observations primarily due to uncertainty about POM deposition, diagenetic processes are represented reasonably well in the optimized model. Therefore, we deemed the optimized model as an appropriate framework for representing the main diagenetic processes on the Louisiana Shelf. Further development of the diagenetic model may include explicit anaerobic reactions, including DNRA and anammox. However, this is beyond the scope of this work.

Comparing optimized parameters to the original parameter set used by Soetaert et al. (1996a) is informative about sediment biogeochemistry on the Louisiana Shelf . The optimization minimized the influence of bioturbation, likely a reflection of the negative impact of hypoxia on sediment biota (Diaz & Rosenberg, 1995; Middelburg & Levin, 2009). This result is also consistent with the dominance of bacteria over invertebrates in the sediment community as observed by Rowe et al. (2002). The small O_2 and NO_3^- inhibition parameters for anaerobic remineralization emphasize the importance of anaerobic processes in the area (Morse and Berner, 1995). This is consistent with observations for Mississippi River plume sediments that suggest a substantial production of reduced substances under low O_2 conditions throughout the Louisiana Shelf (Rowe et al., 2002; Lehrter et al., 2012) and reflects the important role of ODU in the O_2 flux meta-model. The small optimized value for NO_3^- limitation of denitrification indicates that direct denitrification is an important process on the Louisiana Shelf when low O_2 limits coupled nitrification-denitrification (Nunnally et al., 2013). Direct denitrification occurs when NO_3^- is available in bottom waters and tends to increase with increasing NO_3^- concentration (Fennel et al., 2009). The small optimized value of O_2 inhibition on nitrification and the relatively high maximum rate of nitrification compared to the original parameter values are also indications that sediment nitrification is an important process on the Louisiana Shelf, contributing to O_2 consumption in the sediment. This result is also consistent with earlier observations (Lehrter et al., 2012).

We added temperature dependence of remineralization to the original model from Soetaert et al. (1996a). Model results were very sensitive to changes in the remineralization of the fast decaying organic matter pool ($R_2(T)$). The optimum temperature of remineralization (T_{opt}), the remineralization at optimum temperature ($R_2^{T_{opt}}$) and the Q_{10} parameter for the fast decaying organic matter pool (θ_2) all influence $R_2(T)$ and therefore model results are very sensitive to variations in these parameter values.

The meta-model reproduced the results from the optimized diagenetic model remarkably well suggesting that it is possible to use such parameterizations in place of a full, vertically resolved diagenetic model to prescribe sediment-water boundary conditions in biogeochemical circulation models. Previous meta-model parameterizations of diagenetic rates (Middelburg et al., 1996; Soetaert et al., 2000; Gypens et al., 2008) and perturbation response experiments (Rabouille et al., 2001) had similar success. The present method is somewhat different because the goal is to parameterize sediment-water exchanges directly as a function of bottom water conditions. This simplified parameterization method does not require an additional, vertically-integrated sediment layer to track deposited POM as in the method proposed by Soetaert et al. (2000). Although the meta-model is not mass conservative, violation of mass conservation should be minor if the meta-model is used for the system and within the range of conditions that were used for its development. The resulting meta-model exhibits realistic dynamics such as the increase of sediment-water fluxes in summer due to warmer temperature and the time delay between POM deposition and remineralization, the decrease of coupled nitrification-denitrification at low bottom O_2 concentrations and the prominent role of reduced substances (represented by the ODU pool) as an O_2 sink in suboxic conditions.

Perhaps a key difference to other sediment-water parameterizations is the importance of ODU at low O_2, which results in a relatively weak relationship between O_2 flux and bottom O_2 concentration in hypoxic conditions, and the occurrence of O_2 flux in anoxic conditions; in the meta-model, ODU is the dominant source of O_2 consumption in hypoxic conditions and at high temperature (i.e., in summer), independently of bottom O_2 concentration. Previous parameterizations of sediment-water O_2 flux on the Louisiana Shelf considered only SOC and therefore O_2 flux decreased toward zero with decreasing bottom O_2 in the hypoxic range (with a zero intercept for anoxic conditions). However, Lehrter et al. (2012) found an increase of the DIC/O_2 flux ratio with bottom O_2 depletion that they attributed to anaerobic metabolism, i.e. the production of reduced chemical species that accumulate in the sediment, diffuse back and reoxidize in the water column when O_2 becomes available. Justić and Wang (2014) considered the effect of reduced chemical species on biological oxygen demand in their hypoxia model. It represents a significant O_2 sink in bottom waters and needs to be accounted for in the sediment-water O_2 flux parameterization. The O_2 flux meta-model combines SOC and ODU fluxes and is therefore a more realistic representation of O_2 consumption at the sediment-water interface. This formulation assumes instant ODU oxidation in the water column, even in anoxic conditions, whereas oxidation occurs in oxygenated waters only. The time delay between ODU flux and oxidization is therefore missing in the meta-model but is accounted for if the coupled biogeochemical-circulation model carries an O_2 debt in anoxic conditions, as is the case in the models of Fennel et al. (2009, 2013) and Laurent and Fennel (2014).

The meta-model simulates both the O_2 dependence of coupled nitrification-denitrification and direct denitrification, which are also key differences to simple parameterizations of sediment-water fluxes in biogeochemical models. The inhibition of coupled nitrification-denitrification at low O_2 stimulates eutrophication and therefore represents a positive feedback of hypoxia, as observed in Chesapeake Bay and other eutrophic systems (Kemp et al., 1990) and estimated for the global coastal ocean (Rabouille et al., 2001). It is essential to represent this feedback in high N/low O_2 systems such as the Louisiana Shelf. In the NO_3^- meta-model, the inhibition of coupled nitrification-denitrification in hypoxic conditions is partly compensated by the increase in direct denitrification in areas where NO_3^- is available in bottom waters, which results in a nitrate flux to the sediment. On the Louisiana Shelf, this is the case in areas near the Mississippi-Atchafalaya River source, especially in the shallow area near Atchafalaya Bay. The parameterized nitrate uptake by the sediment agrees with observations from the Louisiana Shelf (Gardner et al., 1993; Nunnally et al., 2013). Nunnally et al. (2013) suggest a limited coupling between nitrification and denitrification in the Louisiana Shelf hypoxic zone. Nonetheless, the magnitude of this NO_3^- sink remains much smaller than the NH_4^+ flux to the water column and therefore the overall effect of low bottom O_2 is an enrichment of N in the water column, i.e. a positive feedback on eutrophication.

The meta-model method can be easily implemented in biogeochemical circulation models. However, the method should be applied only on regional scales because different types of bacterial, meio- or macrofaunal communities with various levels of bioturbation are associated with distinct types of substrate, porosity and POM quality and quantity affect POM recycling and thus influence the rates of sediment diagenetic processes locally (Herman et al., 1999). In other words, diagenetic models are region-specific.

5. Summary and conclusions

Benthic-pelagic coupling in biogeochemical circulation models is usually implemented through simple parameterizations or with a diagenetic model. These methods are either too simplistic or computationally very costly. Soetaert et al. (2000) proposed an intermediate method to improve the efficiency of benthic-pelagic coupling in biogeochemical circulation models. Here we presented a simplified version computing a meta-model of sediment-water fluxes for use in a regional biogeochemical model through optimization of a diagenetic model. The method results in a realistic and computationally efficient representation of sediment-water fluxes. Applied to the Louisiana Shelf, the method provides insight in the sediment biogeochemistry of the region, such as the importance of anaerobic processes and reduced substances, the limited level of bioturbation, the occurrence of direct denitrification and the inhibition of coupled nitrification-denitrification in hypoxic conditions. The meta-models represent these Louisiana shelf processes, resulting in more realistic, non-linear interactions between POM deposition, bottom water concentrations and sediment-water fluxes, in particular under hypoxic conditions. A potential limitation of the method is the need for local observations to optimize the diagenetic model.

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References

Aller, Robert, C.: The effects of macrobenthos on chemical properties of marine sediment and overlying water, in Animal-sediment relations, pp. 53–102., 1982.

Boudreau, B. P.: Diagenetic models and their implementation: modelling transport and reactions in aquatic sediments, Springer., 1997.

Boudreau, B. P., Mucci, A., Sundby, B., Luther, G. W. and Silverberg, N.: Comparative diagenesis at three sites on the Canadian continental margin, J. Mar. Res., 56(6), 1259–1284, doi:10.1357/002224098765093634, 1998.

Briggs, K. B., Cartwright, G., Friedrichs, C. T. and Shivarudruppa, S.: Biogenic effects on cohesive sediment erodibility resulting from recurring seasonal hypoxia on the Louisiana shelf, Cont. Shelf Res., 1–10, doi:10.1016/j.csr.2014.11.005, 2014.

Chatterjee, S., Laudato, M. and Lynch, L. A.: Genetic algorithms and their statistical applications: an introduction, Comput. Stat. Data Anal., 22(6), 633–651, doi:10.1016/0167-9473(96)00011-4, 1996.

Cowan, J. L. W. and Boynton, W. R.: Sediment-Water Oxygen and Nutrient Exchanges along the Longitudinal Axis of Chesapeake Bay: Seasonal Patterns, Controlling Factors and Ecological Significance, Estuaries, 19(3), 562–580, doi:10.2307/1352518, 1996.

Dagg, M., Ammerman, J., Amon, R., Gardner, W., Green, R. and Lohrenz, S.: A review of water column processes influencing hypoxia in the northern Gulf of Mexico, Estuaries Coasts, 30(5), doi:10.1007/BF02841331, 735–752, 2007.

Dale, A. W., Bertics, V. J., Treude, T., Sommer, S. and Wallmann, K.: Modeling benthic–pelagic nutrient exchange processes and porewater distributions in a seasonally hypoxic sediment: evidence for massive phosphate release by *Beggiatoa*?, Biogeosciences, 10(2), 629–651, doi:10.5194/bg-10-629-2013, 2013.

Devereux, R., Lehrter, J. C., Beddick, D. L., Yates, D. F. and Jarvis, B. M.: Manganese, iron, and sulfur cycling in Louisiana continental shelf sediments, Cont. Shelf Res., 99, 46–56, doi:10.1016/j.csr.2015.03.008, 2015.

Diaz, R. J. and Rosenberg, R.: Marine benthic hypoxia: a review of its ecological effects and the behavioural responses of benthic macrofauna, Oceanogr. Mar. Biol. an Annu. Rev., 33, 245–303, 1995.

DiToro, D. M.: Sediment flux modeling, Wiley and Sons, New York., 2001.

Eldridge, P. M. and Morse, J. W.: Origins and temporal scales of hypoxia on the Louisiana shelf: Importance of benthic and sub-pycnocline water metabolism, Mar. Chem., 108(3-4), 159–171, doi:10.1016/j.marchem.2007.11.009, 2008.

Eldridge, P. M. and Roelke, D. L.: Origins and scales of hypoxia on the Louisiana shelf: importance of seasonal plankton dynamics and river nutrients and discharge, Ecol Model, 221(7), 1028–1042, doi:10.1016/j.ecolmodel.2009.04.054, 2010.

Fennel, K., Losch, M., Schröter, J. and Wenzel, M.: Testing a marine ecosystem model: sensitivity analysis and parameter optimization, J. Mar. Syst., 28(1-2), 45–63, doi:10.1016/S0924-7963(00)00083-X, 2001.

Fennel, K., Wilkin, J., Levin, J., Moisan, J., O'Reilly, J. and Haidvogel, D.: Nitrogen cycling in the Middle Atlantic Bight: Results from a three-dimensional model and implications for the North Atlantic nitrogen budget, Global Biogeochem. Cycles, 20(3), n/a–n/a, doi:10.1029/2005GB002456, 2006.

Fennel, K., Brady, D., DiToro, D., Fulweiler, R. W., Gardner, W. S., Giblin, A., McCarthy, M. J., Rao, A., Seitzinger, S., Thouvenot-Korppoo, M. and Tobias, C.: Modeling denitrification in aquatic sediments, Biogeochemistry, 93(1-2), 159–178, doi:10.1007/s10533-008-9270-z, 2008.

Fennel, K., Hu, J., Laurent, A., Marta-Almeida, M. and Hetland, R.: Sensitivity of hypoxia predictions for the northern Gulf of Mexico to sediment oxygen consumption and model nesting, J. Geophys. Res. Ocean., 118(2), 990–1002, doi:10.1002/jgrc.20077, 2013.

Fogel, D. B.: An introduction to simulated evolutionary optimization., IEEE Trans. neural networks, 5(1), 3–14, doi:10.1109/72.265956, 1994.

Friedrichs, M. A. M.: A data assimilative marine ecosystem model of the central equatorial Pacific: Numerical twin experiments, J. Mar. Res., 59(6), 859–894, doi:10.1357/00222400160497544, 2001.

Friedrichs, M. A. M., Dusenberry, J. A., Anderson, L. A., Armstrong, R. A., Chai, F., Christian, J. R., Doney, S. C., Dunne, J., Fujii, M., Hood, R., McGillicuddy, D. J., Moore, J. K., Schartau, M., Spitz, Y. H. and Wiggert, J. D.: Assessment of skill and portability in regional marine biogeochemical models: Role of multiple planktonic groups, J. Geophys. Res., 112(C8), C08001, doi:10.1029/2006JC003852, 2007.

Gardner, W. S., Briones, E. E., Kaegi, E. C. and Rowe, G. T.: Ammonium Excretion by Benthic Invertebrates and Sediment-Water Nitrogen Flux in the Gulf of Mexico near the Mississippi River Outflow, Estuaries, 16(4), 799, doi:10.2307/1352438, 1993.

Gypens, N., Lancelot, C. and Soetaert, K.: Simple parameterisations for describing N and P diagenetic processes: Application in the North Sea, Prog. Oceanogr., 76(1), 89–110, doi:10.1016/j.pocean.2007.10.003, 2008.

Herman, P. M. J., Middelburg, J. J., Van de Koppel, J. and Hep, C. H. R.: Ecology of Estuarine Macrobenthos, Adv. Ecol. Res., 29, 195–240, 1999.

Hetland, R. D. and DiMarco, S. F.: How does the character of oxygen demand control the structure of hypoxia on the Texas–Louisiana continental shelf?, J. Mar. Syst., 70(1-2), 49–62, doi:10.1016/j.jmarsys.2007.03.002, 2008.

Hibbert, D. B.: Genetic algorithms in chemistry, Chemom. Intell. Lab. Syst., 19(3), 277–293, doi:10.1016/0169-7439(93)80028-G, 1993.

Justić, D. and Wang, L.: Assessing temporal and spatial variability of hypoxia over the inner Louisiana–upper Texas shelf: Application of an unstructured-grid three-dimensional coupled hydrodynamic-water quality model, Cont. Shelf Res., 72, 163–179, doi:10.1016/j.csr.2013.08.006, 2014.

Justić, D., Rabalais, N. N. and Turner, R. E.: Effects of climate change on hypoxia in coastal waters : a doubled CO2 scenario for the northern Gulf of Mexico, , 41(5), 992–1003, 1996.

Kane, A., Moulin, C., Thiria, S., Bopp, L., Berrada, M., Tagliabue, A., Crépon, M., Aumont, O. and Badran, F.: Improving the parameters of a global ocean biogeochemical model via variational assimilation of in situ data at five time series stations, J. Geophys. Res., 116(C6), C06011, doi:10.1029/2009JC006005, 2011.

Kemp, W. M., Sampou, P., Cafrey, J., Mayer, M., Henriksen, K. and Boynton, W. R.: Ammonium recycling versus denitrification Chesapeake Bay sediments, Limnol. Oceanogr., 35(7), 1545–1563, doi:10.4319/lo.1990.35.7.1545, 1990.

Kolda, T. G., Lewis, R. M. and Torczon, V.: Optimization by direct search: New perspectives on some classical and modern methods, SIAM Rev., 45(3), 385–482, doi:Doi 10.1137/S003614450242889, 2003.

Kuhn, A. M., Fennel, K. and Mattern, J. P.: Model investigations of the North Atlantic spring bloom initiation, Prog. Oceanogr., doi:10.1016/j.pocean.2015.07.004, 2015.

Lehrter, J. C., Murrell, M. C. and Kurtz, J. C.: Interactions between freshwater input, light, and phytoplankton dynamics on the Louisiana continental shelf, Cont Shelf Res, 29(15), 1861–1872, doi:10.1016/j.csr.2009.07.001, 2009.

Lehrter, J. C., Beddick, D., Devereux, R., Yates, D. and Murrell, M.: Sediment-water fluxes of dissolved inorganic carbon, O_2, nutrients, and N_2 from the hypoxic region of the Louisiana continental shelf, Biogeochemistry, 109, 233–252, doi:10.1007/s10533-011-9623-x, 2012.

Li, Y.-H. and Gregory, S.: Diffusion of ions in the sea water and in deep-sea sediments, Geochim. Cosmochim. Acta, 38, 703–714, 1974.

Lin, X., McCarthy, M. J., Carini, S. A. and Gardner, W. S.: Net, actual, and potential sediment–water interface NH4 fluxes in the northern Gulf of Mexico (NGOMEX): Evidence for NH4 limitation of microbial dynamics, , 31, 120–128, doi:10.1016/j.csr.2010.11.012, 2011.

Lin, S. and Morse, J. W.: Sulfate reduction and iron sulfide mineral formation in Gulf of Mexico anoxic sediments, Am. J. Sci., 291(1), 55–89, doi:10.2475/ajs.291.1.55, 1991.

Liu, K.-K., Atkinson, L., Quiñones, R. A. and Talaue-McManus, L.: Biogeochemistry of continental margins in a global context, in Carbon and nutrient fluxes in continental margins, edited by K.-K. Liu, L. Atkinson, R. A. Quiñones, and L. Talaue-McManus, Springer, Berlin., 2010.

McCarthy, M. J., Newell, S. E., Carini, S. a. and Gardner, W. S.: Denitrification Dominates Sediment Nitrogen Removal and Is Enhanced by Bottom-Water Hypoxia in the Northern Gulf of Mexico, Estuaries and Coasts, doi:10.1007/s12237-015-9964-0, 2015.

Middelburg, J. J. and Levin, L. a.: Coastal hypoxia and sediment biogeochemistry, Biogeosciences, 6(7), 1273–1293, doi:10.5194/bg-6-1273-2009, 2009.

Middelburg, J. J. and Soetaert, K.: The role of sediments in shelf ecosystem dynamics, in The global coastal ocean. Multiscale interdisciplinary processes, vol. 13, edited by A. R. Robinson and K. H. Brink, pp. 353–373, John Wiley & Sons, New York., 2005.

Middelburg, J. J., Soetaert, K., Herman, P. M. J. and Heip, C. H. R.: Denitrification in marine sediments : A model study, Global Biogeochem. Cycles, 10(4), 661–673, doi:10.1029/96GB02562, 1996.

Morse, J. W. and Berner, R. A.: What determines sedimentary C/S ratios?, Geochim. Cosmochim. Acta, 59(6), 1073–1077, doi:10.1016/0016-7037(95)00024-T, 1995.

Morse, J. W. and Eldridge, P. M.: A non-steady state diagenetic model for changes in sediment biogeochemistry in response to seasonally hypoxic/anoxic conditions in the “dead zone” of the Louisiana shelf, Mar. Chem., 106(1-2), 239–255, doi:10.1016/j.marchem.2006.02.003, 2007.

Mulsow, S., Boudreau, B. P. and Smith, J. A.: Bioturbation and porosity gradients, Limnol. Oceanogr., 43(1), 1–9, doi:10.4319/lo.1998.43.1.0001, 1998.

Murrell, M. C. and Lehrter, J. C.: Sediment and lower water column oxygen consumption in the seasonally hypoxic region of the Louisiana continental shelf, Estuaries and Coasts, 34, 912–924, doi: 10.1007/s12237-010-9351-9, 2011.

Neubacher, E. C., Parker, R. E. and Trimmer, M.: The potential effect of sustained hypoxia on nitrogen cycling in sediment from the southern North Sea: a mesocosm experiment, Biogeochemistry, 113(1-3), 69–84, doi:10.1007/s10533-012-9749-5, 2012.

Nunnally, C. C., Rowe, G. T., Thornton, D. C. O. and Quigg, A.: Sedimentary Oxygen Consumption and Nutrient Regeneration in the Northern Gulf of Mexico Hypoxic Zone, J. Coast. Res., 63, 84–96, doi:10.2112/SI63-008.1, 2013.

Rabalais, N., Turner, R. E., Dortch, Q., Justić, D., Bierman, V. and Wiseman, W.: Nutrient-enhanced productivity in the northern Gulf of Mexico: past, present and future, Hydrobiologia, 475–476(1), 39–63, doi:10.1023/A:1020388503274, 2002.

Rabouille, C., Mackenzie, F. T. and Ver, L. M.: Influence of the human perturbation on carbon, nitrogen, and oxygen biogeochemical cycles in the global coastal ocean, Geochim. Cosmochim. Acta, 65(21), 3615–3641, doi:10.1016/S0016-7037(01)00760-8, 2001.

Redalje, D. G., Lohrenz, S. E. and Fahnenstiel, G. L.: The Relationship between Primary Production and the Vertical Export of Particulate Organic Matter in a River-Impacted Coastal Ecosystem, Estuaries, 17(4), 829, doi:10.2307/1352751, 1994.

Redfield, A., Ketchum, B. and Richards, F.: The influence of organisms on the composition of sea-water, in The Sea, Vol 2, vol. 2, edited by M. N. Hill, pp. 26–77, John Wiley & Sons, Inc., 1963.

Robson, B., Hamilton, D., Webster, I. and Chan, T.: Ten steps applied to development and evaluation of process-based biogeochemical models of estuaries, Environ. Model. Softw., 23(4), 369–384, doi:10.1016/j.envsoft.2007.05.019, 2008.

Rowe, G. T. and Chapman, P.: Continental shelf hypoxia: some nagging questions, Gulf Mex. Sci., 2, 155–160, 2002.

Rowe, G. T., Cruz Kaegi, M. E., Morse, J. W., Boland, G. S. and Escobar Briones, E. G.: Sediment community metabolism associated with continental shelf hypoxia, Northern Gulf of Mexico, Estuaries, 25(6), 1097–1106, doi:10.1007/BF02692207, 2002.

Schartau, M. and Oschlies, A.: Simultaneous data-based optimization of a 1D-ecosystem model at three locations in the North Atlantic: Part I—Method and parameter estimates, J. Mar. Res., 61(6), 765–793, doi:10.1357/002224003322981147, 2003.

Soetaert, K. and Herman, P. M. J.: Nitrogen dynamics in the Westerschelde estuary (SW Netherlands) estimated by means of the ecosystem model MOSES, Hydrobiologia, 311(1-3), 225–246, doi:10.1007/BF00008583, 1995.

Soetaert, K. and Petzoldt, T.: Inverse Modelling, Sensitivity and Monte Carlo Analysis in R Using Package FME, J. Stat. Softw., 33(3), doi:10.18637/jss.v033.i03, 2010.

Soetaert, K., Herman, P. M. J. and Middelburg, J. J.: A model of early diagenetic processes from the shelf to abyssal depths, Geochim. Cosmochim. Acta, 60(6), 1019–1040, doi:10.1016/0016-7037(96)00013-0, 1996a.

Soetaert, K., Herman, P. M. J. and Middelburg, J. J.: Dynamic response of deep-sea sediments to seasonal variations: A model, Limnol Ocean., 41(8), 1651–1668, 1996b.

Soetaert, K., Herman, P. M. J., Middelburg, J. J. and Heip, C.: Assessing organic matter mineralization, degradability and mixing rate in an ocean margin sediment (Northeast Atlantic) by diagenetic modeling, J. Mar. Res., 56(2), 519–534, doi:10.1357/002224098321822401, 1998.

Soetaert, K., Middelburg, J. J., Herman, P. M. J. and Buis, K.: On the coupling of benthic and pelagic biogeochemical models, Earth-Science Rev., 51(1-4), 173–201, doi:10.1016/S0012-8252(00)00004-0, 2000.

Ward, B. a., Friedrichs, M. a. M., Anderson, T. R. and Oschlies, A.: Parameter optimisation techniques and the problem of underdetermination in marine biogeochemical models, J. Mar. Syst., 81(1-2), 34–43, doi:10.1016/j.jmarsys.2009.12.005, 2010.

Wilson, R. F., Fennel, K. and Paul Mattern, J.: Simulating sediment–water exchange of nutrients and oxygen: A comparative assessment of models against mesocosm observations, Cont. Shelf Res., 63, 69–84, doi:10.1016/j.csr.2013.05.003, 2013.

Wood, C. C., Statham, P. J., Kelly-Gerreyn, B. a. and Martin, A. P.: Modelling macronutrients in shelf sea sediments: fitting model output to experimental data using a genetic algorithm, J. Soils Sediments, 14(1), 218–229, doi:10.1007/s11368-013-0793-0, 2013.

Table 1. Bottom water conditions at stations Z02 and Z03 in 2006. These data are used as forcing conditions during the optimization of the diagenetic model. POM deposition flux (FPOM) was not measured; FPOM monthly climatologies were calculated for station Z02 and Z03 from a multiyear simulation with a biogeochemical circulation model (see Section 2.3).

Station	Date	F_{POM}	Temperature	NO_3^-	NH_4^+	O_2
		mmol N m^{-2} d^{-1}	°C	mmol m^{-3}	mmol m^{-3}	mmol m^{-3}
Z02	April	3.53	21.6	7.16	0.58	60.2
	June	2.19	24.0	8.61	7.93	0.0
	September	0.95	29.6	8.45	0.32	16.0
Z03	April	1.36	21.7	1.50	0.47	67.9
	June	1.20	25.7	1.90	2.40	137.9
	September	0.44	29.1	5.63	0.82	118.4

Table 2. Diagenetic model parameters. The 20 parameters that were optimized are indicated with a + sign. The original values are from Soetaert et al. (1996a); an asterisk indicates values that are identical in the optimized parameter set.

Symbol	Value			Parameter description	Units	Range
	optimized	original				
H	*	10		Active sediment depth	cm	–
Φ_0	*	0.8		Porosity at surface		–
$\Phi\infty$	*	0.7		Porosity at depth H		–
Φ_{coef}	*	4.0		Porosity decay coefficient	cm^{-1}	–
w_{sed}	0.416	0.022	(+)	Burial velocity	cm y^{-1}	0.05–1
D_{NH4}	*	0.847		Diffusion coefficient for ammonium at 0°C	cm^2 d^{-1}	–
D_{NO3}	*	0.845		Diffusion coefficient for nitrate at 0°C	cm^2 d^{-1}	–
D_{O2}	*	0.955		Diffusion coefficient for oxygen at 0°C	cm^2 d^{-1}	–
D_{ODU}	*	0.842		Diffusion coefficient for ODU at 0°C	cm^2 d^{-1}	–
a_{NH4}	*	0.0336		T-dependent coefficient for ammonium diffusion	cm^2 d^{-1} (°C)$^{-1}$	–
a_{NO3}	*	0.0303		T-dependent coefficient for nitrate diffusion	cm^2 d^{-1} (°C)$^{-1}$	–
a_{O2}	*	0.0386		T-dependent coefficient for oxygen diffusion	cm^2 d^{-1} (°C)$^{-1}$	–
a_{ODU}	*	0.0242		T-dependent coefficient for ODU diffusion	cm^2 d^{-1} (°C)$^{-1}$	–
z_{bio}	1.0	5.0	(+)	Depth of bioturbated layer	cm	1–7
$Dbio_0$	8.784	1.53	(+)	Bioturbation "diffusivity"	cm^2 y^{-1}	1–65
Db_{coeff}	*	1.0		Exponential decay below bioturbated layer	cm^{-1}	–
R_1^{Topt}	0.0213	0.02	(+)	Remineralization at T_{opt} for slow decaying OM1 pool	yr^{-1}	10^{-4}–10^{-1}
R_2^{Topt}	2.821	2.0	(+)	Remineralization at T_{opt} for fast decaying OM2 pool	yr^{-1}	0.1–30
PB	0.00	0.05	(+)	Part of ODUs permanently buried per day	d^{-1}	0–0.95
k_{O2}	20.0	3.0	(+)	Half-saturation, O$_2$ limitation on aerobic remineralization	μmolO$_2$ L^{-1}	0.1–20
kin_{odu}	0.1	5.0	(+)	Half-saturation, O$_2$ inhibition on anaerobic remin.	μmolO$_2$ L^{-1}	0.1–20
ox_{odu}	11.45	20.0	(+)	Maximum oxidation rate of ODUs	day^{-1}	0.1–50
k_{odu}	20.0	1.0	(+)	Half-saturation, O$_2$ in ODU oxidation	μmolO$_2$ L^{-1}	0.1–20
Nit	50.0	20.0	(+)	Maximum nitrification rate	day^{-1}	0.05–50
k_{nit}	0.1	1.0	(+)	Half-saturation, O$_2$ inhibition on nitrification	μmolO$_2$ L^{-1}	0.1–10
k_{dnf}	1.0	30.0	(+)	Half-saturation, nitrate limitation of denitrification	μmolNO$_3$ L^{-1}	1–60
kin_{dnf}	30.0	10.0	(+)	O$_2$ inhibition of denitrification	μmolO$_2$ L^{-1}	1–30
kin_{anox}	0.1	5.0	(+)	Half-saturation, nitrate inhibition of anaerobic remin.	μmolO$_2$ L^{-1}	0.1–20
θ_{r1}	3.0	–	(+)	Q$_{10}$ parameter for r$_1$		2–3
θ_{r2}	3.0	–	(+)	Q$_{10}$ parameter for r$_2$		2–3
θ_{bio}	2.0	–	(+)	Q$_{10}$ parameter for the bioturbation of solids		2–3
T_b	30.0	–	(+)	Base temperature for Q$_{10}$ relationship	°C	20–30
α_0	0.0002	–	(+)	Non-local mixing coefficient	yr^{-1}	0–100

Table 3. Cost $F(\boldsymbol{p})$, calculated using Equation 3, for each variable type at station Z02 and Z03. Simulations were run with the parameter set from Soetaert et al (1996a) (original) and with the optimized parameter set (baseline). Additional optimizations were carried out for each station independently (site-specific), for each station using sediment-water fluxes only (site-specific, fluxes only), and including POM depositional flux in the optimization (site-specific, fluxes only, + F_{POM}).

Optimization	Station	F_{O_2}	$F_{NH_4^+}$	$F_{NO_3^-}$	NH_4^+ profiles	Total
Original	Z02	0.1	366.2	107.8	1.5	475.6
	Z03	3.1	2788.3	1388.4	9.0	4188.8
	Total	3.2	3154.5	1496.2	10.5	4664.4
Baseline	Z02	0.2	8.6	52.6	1.5	62.9
	Z03	3.8	34.1	137.0	8.1	183.0
	Total	4.0	42.7	189.6	9.6	245.9
Site-specific	Z02	0.3	6.7	4.3	6.0	17.3
	Z03	3.9	25.7	134.0	8.9	172.5
	Total	4.2	32.4	138.3	14.9	189.8
Site-specific, flux only	Z02	0.4	5.0	3.8	-	9.3
	Z03	3.5	20.7	116.9	-	141.1
	Total	3.9	25.7	120.7	-	150.3
Site-specific, flux only + F_{POM}	Z02	0.6	0.2	0.0	-	0.8
	Z03	5.4	2.9	68.5	-	76.8
	Total	6.0	3.1	68.5	-	77.6

Table 4. Meta-model coefficients for sediment O_2 consumption (F_{O2}), NH_4 flux ($F_{NH_4^+}$) and NO_3^- flux ($F_{NO_3^-}$). The form of the relationship is given in Eq. 4. For each flux, the average contribution of each input variable is indicated as well as the dominant direction of its effect. A positive effect promotes a weaker flux into the sediment or a larger flux to the water column (depending on the direction of the flux) whereas a negative effect leads to a larger sink into the sediment or a weaker flux to the water column. +/– indicates that the effect's direction varies as a function of the variable. The contributions were calculated from standardized coefficients. Bold values indicate variables contributing > 10% in average.

		Constant	F_{POM} mmol N m^{-2} d^{-1}	Salinity	Temperature °C	NH_4^+ mmol m^{-3}	NO_3^- mmol m^{-3}	O_2 mmol m^{-3}
Data range			0.1 – 62.1	0 – 36.4	15.1 – 36.0	0.1 – 24.7	0 – 161.2	0 – 475.1
F_{O2}	x_i	22.1151	-1.3381	0.8138	-7.1247	0.4592	-0.8055	-0.0721
	x_i^2		0.0286	0.0868	0.3668	-0.2074	0.0229	-0.0001
	x_i^3		-0.0001	-0.0023	-0.0069	0.0112	-0.0001	0.0000
	Contribution (%)		5.0	**20.3**	**55.4**	1.9	**10.4**	6.9
	Effect direction		–	+	–	+/–	+/–	+/–
F_{NH4}	x_i	-10.8192	0.0740	-0.0833	2.0967	-0.2221	0.0836	-0.0283
	x_i^2		0.0023	-0.0064	-0.0996	0.0500	-0.0024	0.0002
	x_i^3		-0.0001	0.0002	0.0016	-0.0023	0.0000	-0.0000
	Contribution (%)		1.5	**11.4**	**59.1**	3.3	5.4	**19.3**
	Effect direction		+/–	–	+	+/–	+/–	–
F_{NO3}	x_i	3.6115	-0.0071	0.0463	-0.5613	0.1142	-0.0134	0.0144
	x_i^2		-0.0014	-0.0035	0.0238	-0.0209	0.0001	-0.0001
	x_i^3		0.0000	0.0001	-0.0003	0.0008	-0.0000	0.0000
	Contribution (%)		0.8	**12.8**	**54.1**	5.2	2.6	**24.5**
	Effect direction		–	+/–	–	+/–	–	+

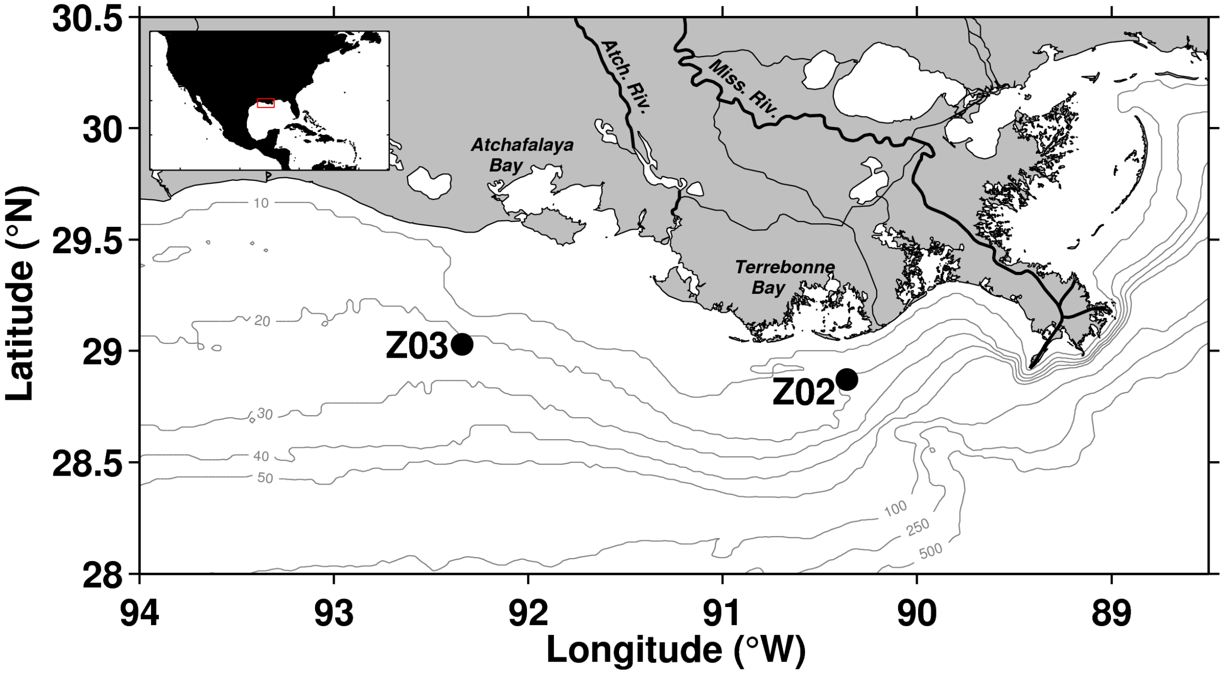


Figure 1. Map of the Louisiana Shelf showing the location of sample collection sites Z02 and Z03.

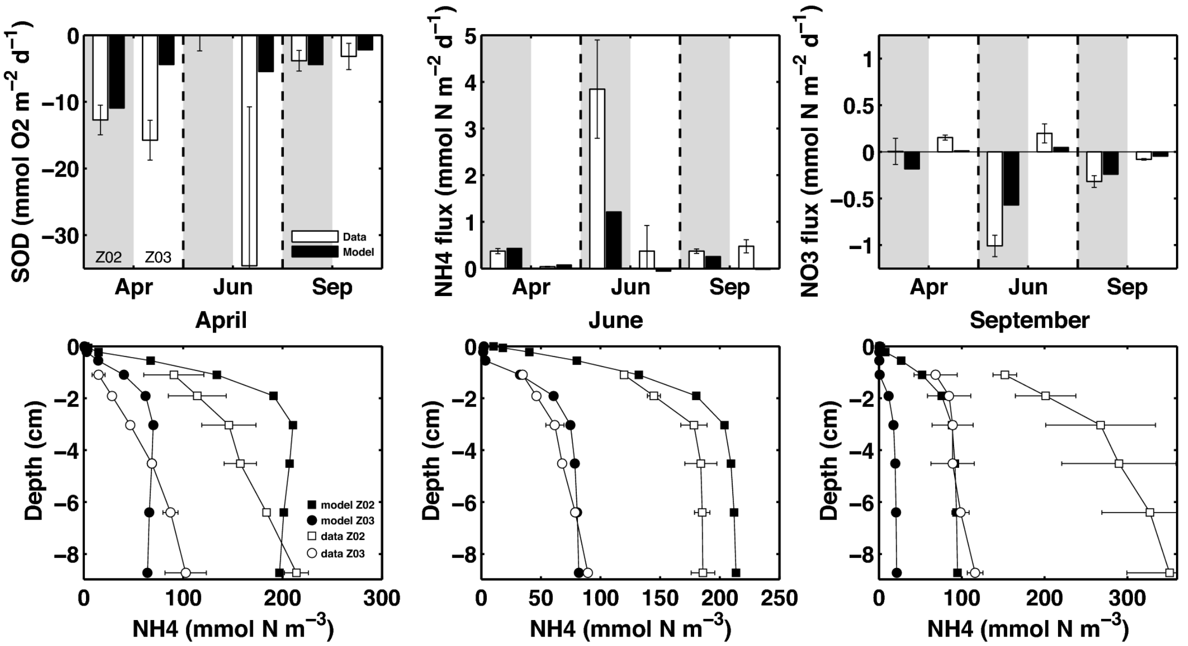


Figure 2. Model-data comparison of sediment water fluxes (top row) and NH_4^+ profiles (bottom row) for sites Z02 and Z03. Simulations use the optimized parameter set (baseline).

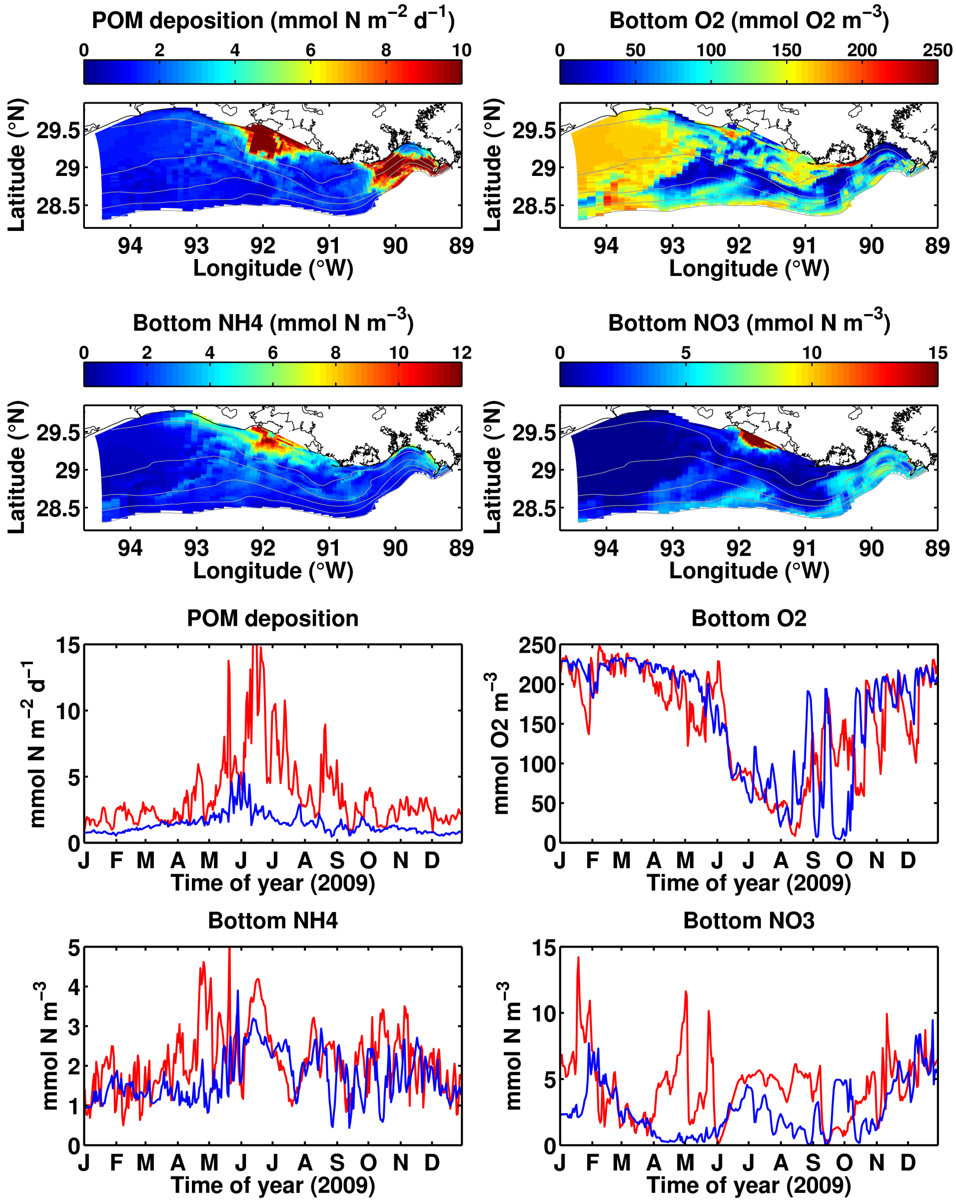


Figure 3. Spatial (top) and temporal (bottom) POM depositional flux and bottom water O_2, NH_4^+ and NO_3^- concentrations in the biogeochemical circulation model. The upper panels represent a snapshot of bottom water conditions on August 15th, 2009 and the lower panels time series at stations Z02 and Z03. This dataset is used to force the diagenetic model in the meta-modeling

procedure (Section 2.2), to compute spatial fluxes with the meta-model (Figure 8) and to compare the meta-model and H&D parameterizations (Figure 12).

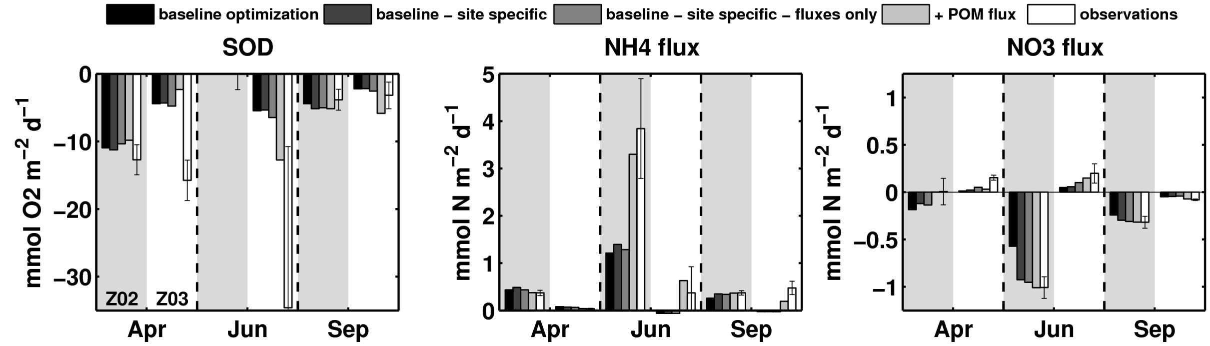


Figure 4. Model-data comparison of sediment water fluxes at stations Z02 and Z03 for several different optimization schemes (baseline includes all constraints).

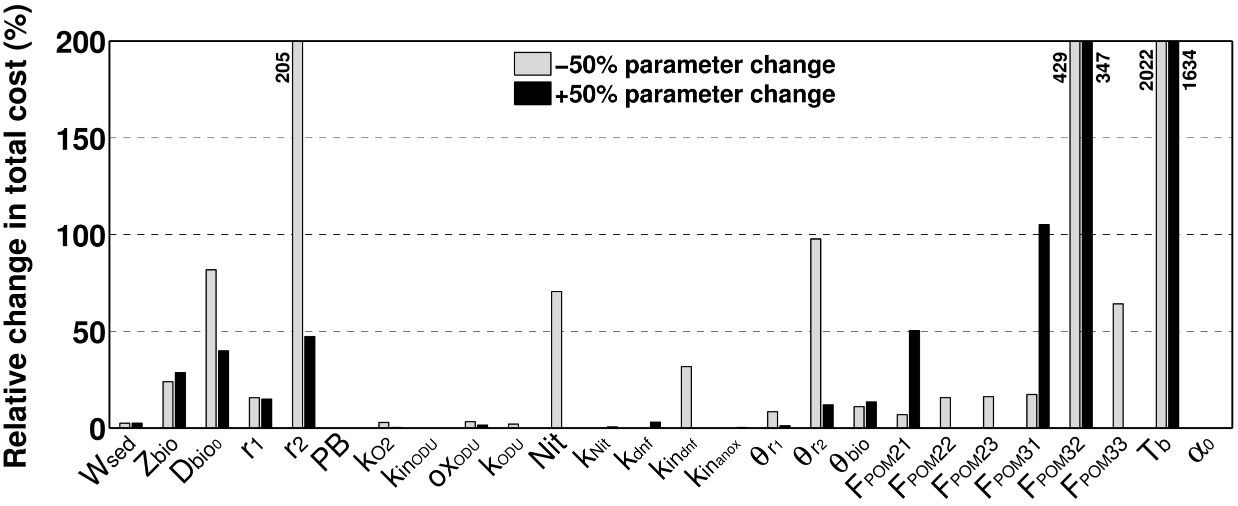


Figure 5. Sensitivity of model results to parameter variation.

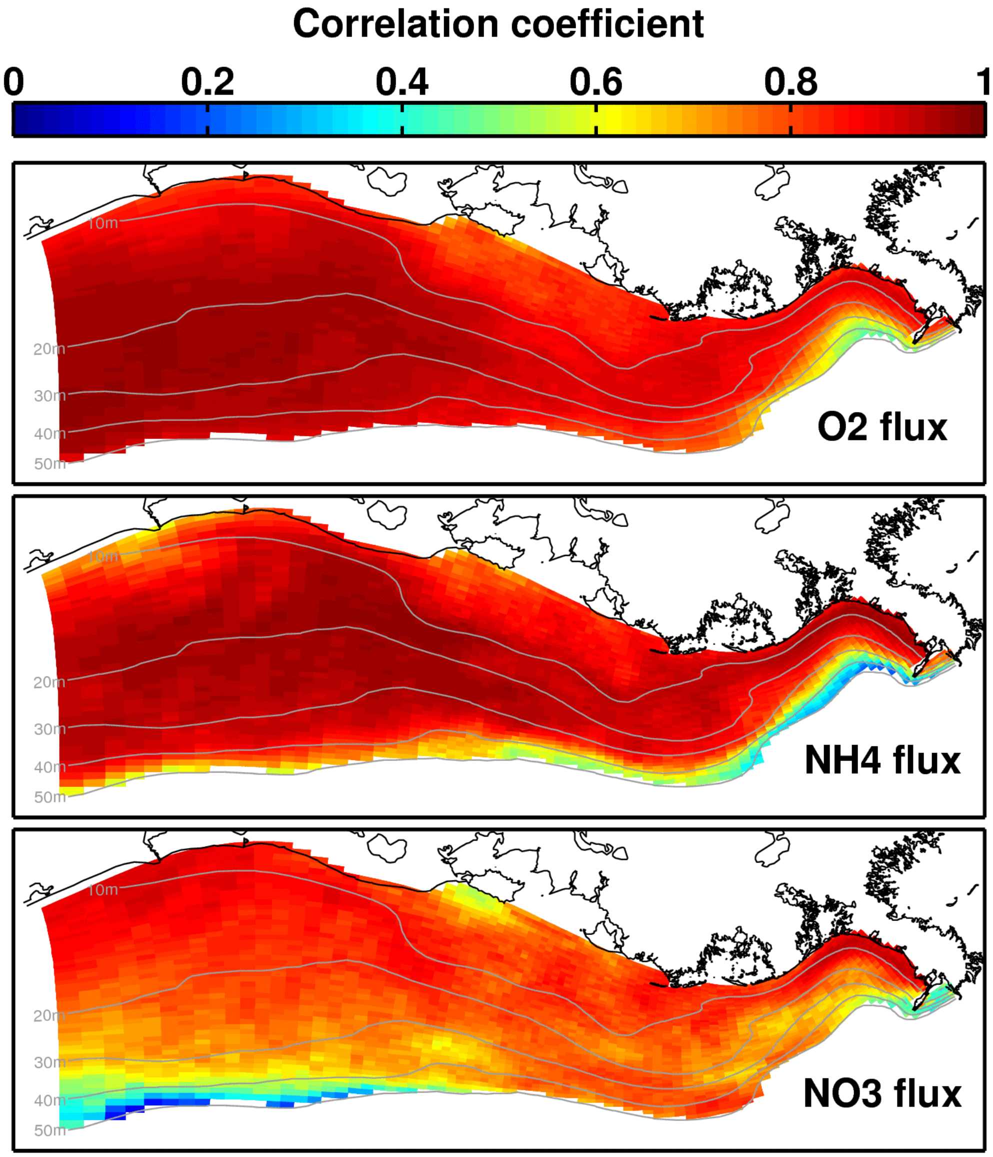
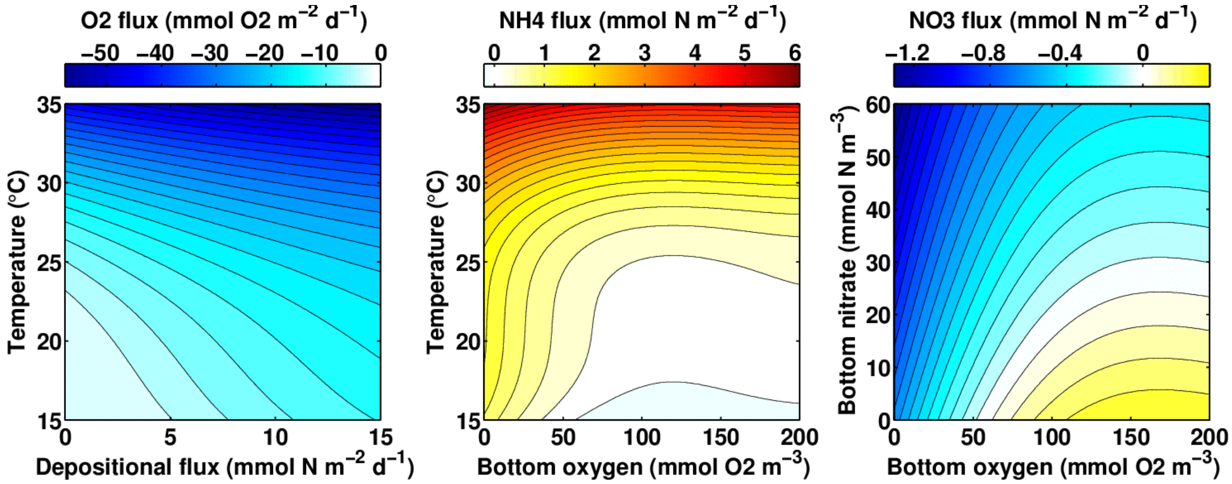


Figure 6. Correlation coefficients between time-dependent diagenetic model simulations and the parameterized fluxes for each location on the Louisiana Shelf.



845 Figure 7. Influence of selected contributors to O_2, NH_4^+ and NO_3^- fluxes. Negative fluxes (blue shades) are into the sediment and positive fluxes (orange shades) are out of the sediment.

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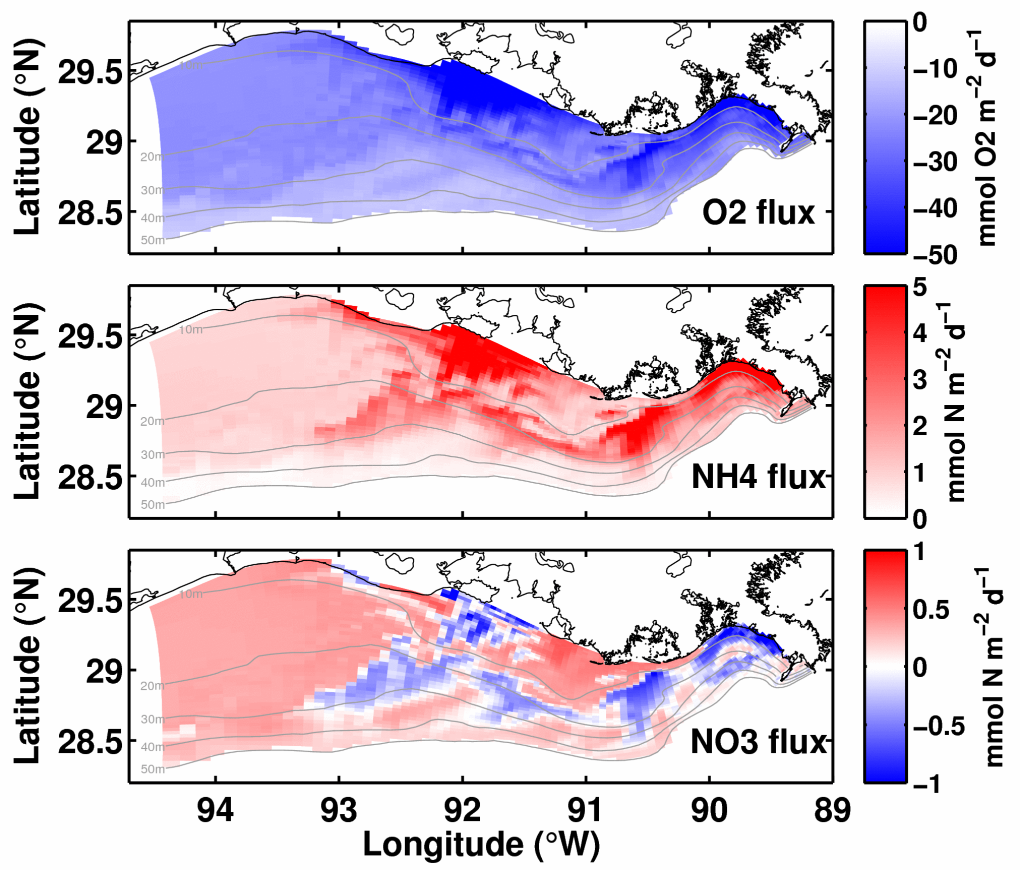

Figure 8. Spatial distribution of parameterized O_2, NH_4^+ and NO_3^- fluxes on August 15th, 2009. Negative fluxes (blue) are into the sediment.

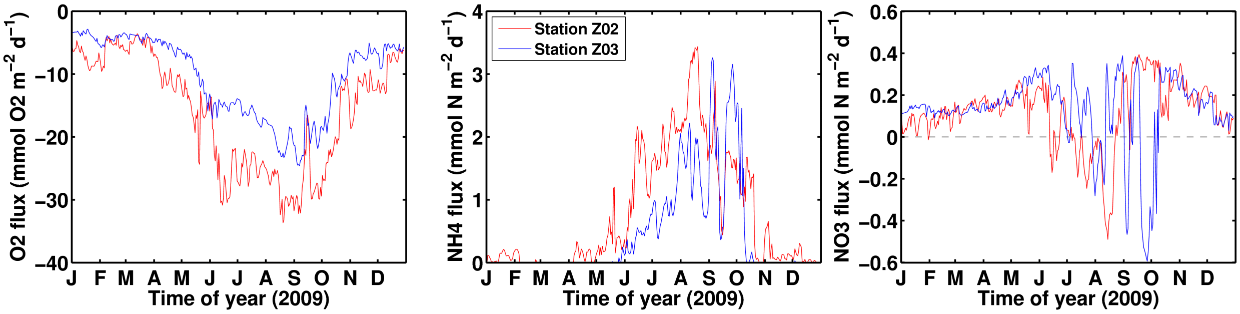

Figure 9. Temporal variability of parameterized O_2, NH_4^+ and NO_3^- fluxes at station Z02 and Z03 in 2009. Negative fluxes are into the sediment.

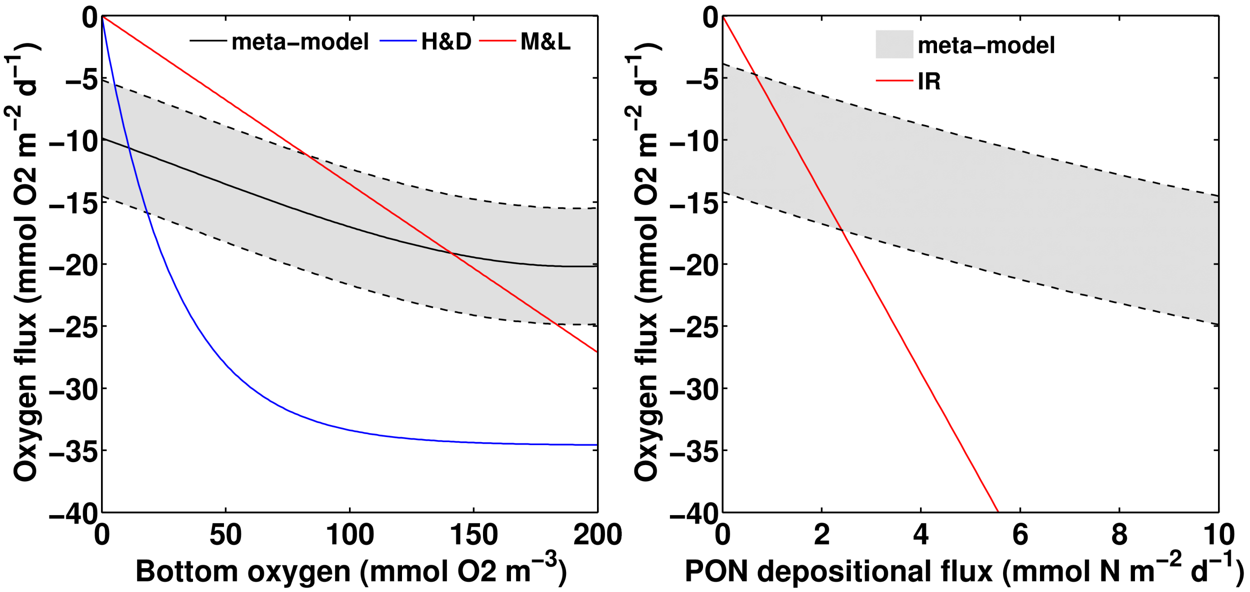

Figure 10. O_2 flux in the meta-model compared to that from the IR, H&D and M&L parameterizations as a function of bottom O_2 concentration (left) and of POM depositional flux (right). The grey area and the black line on the left panel corresponds to the variation in O_2 flux when $1 < F_{POM} < 10$ mmol N m^{-2} d^{-1} and $F_{POM} = 5$ mmol N m^{-2} d^{-1}, respectively. The grey area on the right panel corresponds to the variation in O_2 flux when bottom O_2 concentration range from 0 to 200 mmol O_2 m^{-3}. The comparison between H&D, M&L and SOC observations can be found in Fennel et al (2013) and Yu et al (2015).

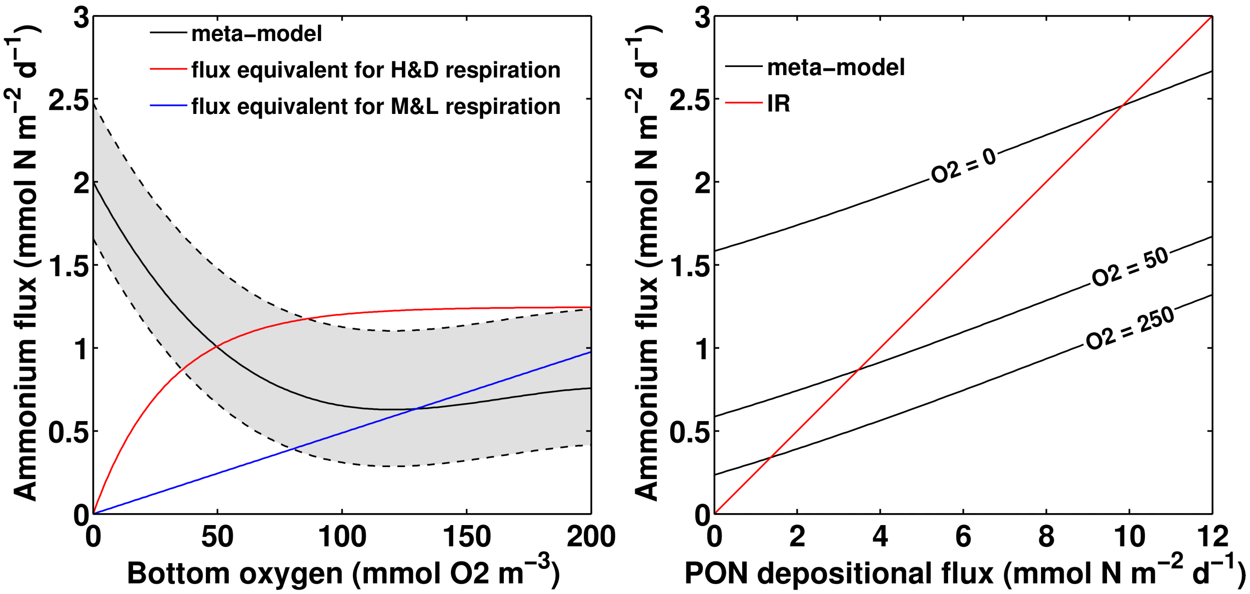

Figure 11. NH_4^+ flux in the meta-model compared with that from the IR, H&D and M&L parameterizations. NH_4^+ flux is represented as a function of (left) bottom O_2 concentration and (right) PON depositional flux. The grey area and the black line on the left panel correspond to the variation in O_2 flux when $1 < F_{POM} < 10$ mmol N m^{-2} d^{-1} and $F_{POM} = 5$ mmol N m^{-2} d^{-1}, respectively. The black lines on the right indicate the O_2 flux at bottom O_2 concentrations of 0, 50 and 250 mmol O_2 m^{-3}.

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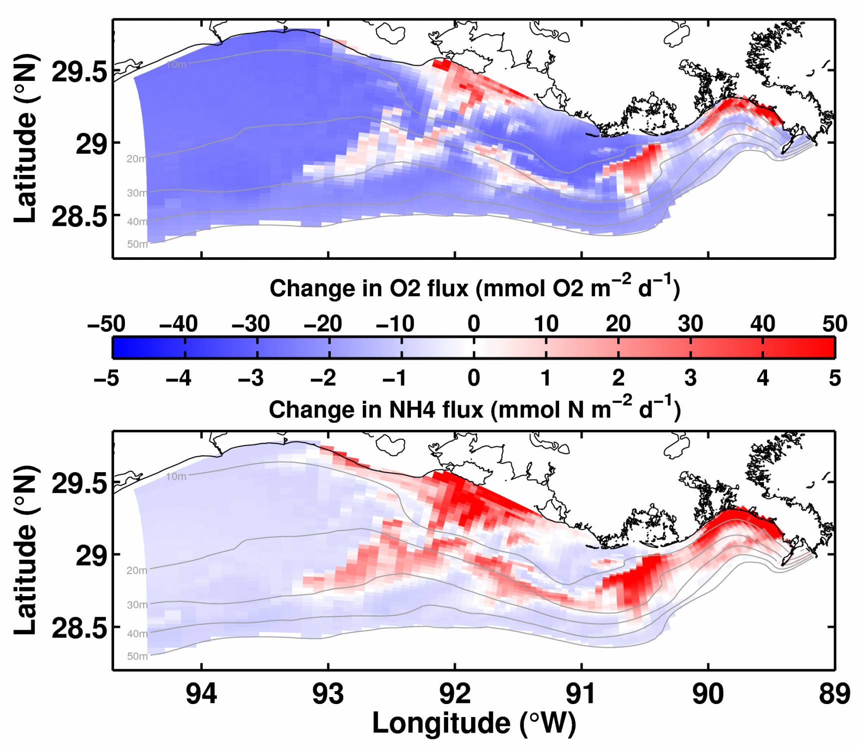

Figure 12. Difference between parameterized oxygen (top panel) and ammonium (bottom panel) fluxes and fluxes simulated with the H&D parameterization in August 15th, 2009.