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Parameterization of biogeochemical sediment–water fluxes using in-situ measurements and a steady-state 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 by combining in situ measurements, a steady state diagenetic model and a parameter optimization method. 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.

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1 Introduction

Sediment biogeochemistry represents a major component of elemental cycling on continental margins (Middelburg and 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 (Xu and Hood, 2006). For instance, a proportion of the deposited nitrogen (N) is lost as biologically unavailable N gas (N_2) through denitrification in the sediment (Fennel et al., 2006). Denitrification represents a major removal pathway for N in coastal areas (Fennel et al., 2009) and buffers the effects of excessive N loads in eutrophic systems (Seitzinger and 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 ($O_2 < 62.5\,\mathrm{mmol\,O_2\,m^{-3}}$) 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 (NO_3)/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

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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.

Vertically integrated or depth-resolved mechanistic models of diagenesis are more realistic representations of sediment biogeochemistry (Rabouille and Gaillard, 1991; Soetaert and 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 mineralization 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).

In order to merge the efficiency of simple sediment–water flux parameterizations with the realism of mechanistic sediment biogeochemical models, we apply here a method for parameterizing sediment–water fluxes in coupled biogeochemical circulation models, using in-situ measurements, a mechanistic model of early diagenesis and a pa-

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rameter 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, refractory content), 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 steady-state 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 similar to the approach proposed by Soetaert et al. (2000). Finally, we compare the fluxes parameterized with the meta-model and with previous relationships used for the Louisiana Shelf.

2 Materials and methods

2.1 Observations

The observations used for optimization of the diagenetic model parameters were collected at two locations along the 20 m isobath on the Louisiana Shelf (Fig. 1) during 3 process leg 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 (near shelf survey station C06) 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 (near shelf survey station H04) 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 (Fig. 2). 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 10^5 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 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 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 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 oxygen 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, and the O_2 sink in bottom waters necessary to oxidize any ODU efflux from the sediment.

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

$$R_i(T) = R_i^{T_{opt}} \times \theta^{(T - T_{opt})/10} \quad (1)$$

where $R_i(T)$ is the rate of the process i at temperature T, $R_i^{T_{opt}}$ is the rate at optimum temperature T_{opt} (i.e., $R_1^{T_{opt}}$ and $R_2^{T_{opt}}$ for remineralization rates and $Dbio_0$ for bioturbation, Table 2) and θ is the Q_{10} factor. This modification allows for the representation of temperature-dependence of microbial processes in the sediment, which is known to be important in coastal systems (see, e.g., Fig. 5 in Wilson et al., 2013).

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

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

where $I(z)$ is the irrigation at depth z, C_{ow} and $C(z)$ 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 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).

The model has a total of 36 parameters (Table 1). Sediment porosity parameters were chosen to obtain a porosity profile that is within the range observed on the Louisiana Shelf. Given the lack of observations on the labile and refractory fraction of OC and on their C:N ratio, these values were set following Wilson et al. (2013). The exponential decay coefficient for bioturbation was set as in the original model (Soetaert et al., 1996a). Solute-specific diffusion coefficients (D_i^T) at ambient temperature T were calculated following Soetaert et al. (1996a) and Li and Gregory (1974) such that $D_i^T = D_i + \alpha_i T$, where D_i is the solute-specific diffusion coefficient at 0 °C and α_i

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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.

The diagenetic model was run to steady state for each time and location where observations were available, i.e. April, June and September 2006 at station Z02 and Z03. 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 observations of POM depositional flux were not available, POM depositional fluxes were prescribed using monthly climatologies calculated for station Z02 and Z03 from a multiyear simulation with a biogeochemical circulation model (see Sect. 2.2.3).

2.2.2 Parameter optimization

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 technique was successfully used for the optimization of parameters of Soetaert et al.'s (1996a) diagenetic model (Wilson et al., 2013; Wood et al., 2013). 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 $n/2$ individuals, i.e. those with the lowest cost, become the parent population and a next generation of $n/2$ 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 $n = 30$ population

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members and $k = 200$ 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 concentrations and sediment–water fluxes) using a cost function that includes all model variables at the 6 locations/times. The cost represents the fitness of an individual (i.e. parameter set) during the evolutionary optimization process. The cost function F for the parameter set $\boldsymbol{p}$ was calculated as follows:

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

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; $\sigma_{s,i}^2$ is the observation SD; 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 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

Meta-modeling parameterizes sediment–water fluxes by means of a multivariate regression model that relates bottom water conditions to sediment–water fluxes, and was used here as proposed by Soetaert et al. (2000) to parameterize Louisiana Shelf fluxes at the sediment–water interface. This technique combines the simplicity and efficiency of a bottom water parameterization with the realism of a diagenetic model.

The diagenetic model was run to steady state using the single parameter set optimized for the Louisiana Shelf and a wide range of bottom water forcing conditions. These conditions were collected randomly out of a model-based dataset representative of bottom water conditions on the Louisiana Shelf (described in more detail below). In total, 100 000 sets of realistic bottom water conditions, namely combinations of temperature, salinity, NO_3, NH_4, O_2 and POM depositional flux, were used. Multivariate regressions were then calculated for each flux variable to relate bottom water conditions (model inputs) with each sediment–water flux (model output). Each regression model is expressed as follows:

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

where each x_i corresponds to an explanatory variable, 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.

As mentioned already above, POM depositional fluxes are required to force the diagenetic model, but are not available in the observation dataset. Furthermore, the meta-modeling procedure requires a large number of representative bottom water conditions – significantly more than are available from observations. In order to fill these two data

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gaps, we sample the output from a realistic biogeochemical circulation model based on the Regional Ocean Modeling System (ROMS). The simulation is described in Fennel et al. (2013) (case B20clim) and covers the period from 2004 to 2009. For details on the model set up and validation we refer the reader to Fennel et al. (2013).

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 there parameterizations represent SOC and NH_4 flux only. The first, referred to as IR, assumes instantaneous remineralization of deposited PON into NH_4 while a fraction of N is lost through denitrification. The other two parameterizations assume that SOC depends on bottom water O_2 and temperature only and ignore POM deposition. One, referred to as H&D, is from Hetland and DiMarco (2008) and the other, referred to as M&L, is from Murrell and Lehrter (2012) with a temperature-dependence added by Fennel et al. (2013).

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 SDs of the observations (Fig. 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

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a very large SD in April at station Z03 and therefore did not influence the optimization. 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 (Fig. 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 (Fig. 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 SDs for this case and therefore this NH_4 sediment profile had only a small influence on the optimization.

Within the optimized parameter set, several parameter values are 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 (PB) does not occur in the optimized model. Conversely, the optimized Q_{10} factors for the remineralization rates 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 rates 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 (Fig. 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 (Fig. 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 (Fig. 2). The best agreement between simulated and observed sediment–water fluxes is achieved by including POM depositional fluxes as additional parameter to optimize (Fig. 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, the RMSE for sediment NH_4 concentrations increases significantly, from 87.59 $\mathrm{mmol\,N\,m^{-2}\,d^{-1}}$ for the baseline case to 174.45 $\mathrm{mmol\,N\,m^{-2}\,d^{-1}}$ (site-specific, flux only) and 111.86 $\mathrm{mmol\,N\,m^{-2}\,d^{-1}}$ (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.

The optimized model is sensitive to several parameters related to the remineralization of the fast decaying organic matter pool ($R_2(T)$) and to the POM deposition rates (F_{POM}) (Fig. 4). The total cost is very sensitive to the POM deposition rate at station Z03 ($F_{POM}3_x$), but not at station Z02 ($F_{POM}2_x$, Fig. 4); 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. To a lesser extent, model results were also sensitive to the bioturbation diffusivity ($Dbio_0$) and to the maximum rate of nitrification (Nit).

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3.2 Meta-modeling parameterization

A meta-model of sediment–water fluxes was derived using simulations with the optimized diagenetic model, as described in Sect. 2.2.3. The coefficients of the meta-model parameterizations for O_2, NH_4 and NO_3 sediment–water fluxes are presented in Table 4. Each parameterization is able to reproduce the sediment–water fluxes simulated with the diagenetic model (Fig. 5). The agreement between simulated and parameterized fluxes is excellent for O_2 ($r^2 = 0.99$) and NH_4 ($r^2 = 0.95$) and very good for NO_3 fluxes ($r^2 = 0.63$) (Fig. 5).

The meta-model for O_2 flux is dominated by POM deposition with O_2 flux depending almost linearly on POM deposition (Table 4). Temperature also influences O_2 flux primarily above 20 °C (Fig. 6). The meta-model for NH_4 flux is similar in that NH_4 flux is also dominated by POM deposition with a temperature effect above 20 °C. However, bottom water O_2 has a growing effect on NH_4 flux under hypoxic conditions (Table 4, Fig. 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. In contrast to O_2 and NH_4 fluxes, the meta-model for NO_3 flux is independent of POM deposition. NO_3 concentration, O_2 concentration and temperature in bottom waters contribute more evenly to this relationship (Table 4). Bottom water NO_3 and O_2 concentrations control both the direction and intensity of NO_3 flux in the meta-model. With oxygenated bottom waters, NO_3 flux is essentially controlled by 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 (Fig. 6).

By using simulated bottom water conditions from our biogeochemical circulation model as input for the meta-models we can assess the spatial and temporal variability in parameterized sediment–water fluxes over the Louisiana Shelf (see Fig. S1). Sediment–water fluxes were computed from the meta-model at the time of the LUM-

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CON hypoxia survey in July 2009 (Fig. 7) and throughout 2009 at station Z02 and Z03 (Fig. 8). The spatial distribution of parameterized O_2 and NH_4 fluxes are relatively similar (Fig. 7), with large fluxes near Atchafalaya Bay and the Mississippi River delta where POM deposition is high ($> 5\,mmol\,N\,m^{-2}\,d^{-1}$, Fig. S1). Patches of moderate NH_4 flux ($1–3\,mmol\,N\,m^{-2}\,d^{-1}$) occur southwest of Terrebonne Bay and further west on the shelf where bottom waters are hypoxic (Fig. S1). 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 (Fig. 7). NO_3 flux into the sediment in the deep offshore areas is driven by high bottom water NO_3 concentrations.

The time series at stations Z02 and Z03 indicate high temporal variability in parameterized sediment–water fluxes (Fig. 8) that are driven by rapid changes in bottom water conditions (Fig. S1). O_2 flux follows POM deposition closely at both stations. The difference in the magnitude of O_2 flux is large between the two stations (Fig. 8) due to the spatial variations in POM deposition (Fig. S1). A similar pattern occurs for NH_4 flux at station Z02 (Fig. 8). However, NH_4 flux at station Z03 is uncorrelated with POM deposition and mostly driven by changes in bottom O_2 concentrations (Fig. S1). 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 both stations result in a switch from efflux of NO_3 from the sediment to influx of NO_3 into the sediment (Fig. 8).

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 is relatively insensitive to bottom water O_2 concentrations in the meta-model (Fig. 9). Since the magnitude of O_2 flux is highly

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correlated with POM depositional flux in the meta-model, IR and the meta-model are relatively similar (Fig. 9). However, except at low POM deposition, O_2 flux is significantly lower in the meta-model.

The NH_4 flux parameterized with the meta-model differs significantly from the NH_4 flux calculated from H&D and M&L (Fig. 10). POM deposition is the main driver of NH_4 flux in the meta-model whereas the equivalent fluxes in the H&D and M&L parameterizations are insensitive to depositional flux. Also, in the meta-model NH_4 flux to the water column increases in hypoxic conditions. Even at low POM deposition, NH_4 flux is much larger in the meta-model than in the three previous parameterizations when bottom O_2 is low. However, when O_2 is available ($O_2 > 50\,\mathrm{mmol\,O_2\,m^{-3}}$), NH_4 flux is relatively similar between the meta-model and IR (Fig. 10).

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 (see Fig. S2). O_2 fluxes are larger in the meta-model in the areas of high POM deposition near the Mississippi and Atchafalaya river mouths and outside Terrebonne Bay (see Fig. S1). O_2 fluxes are smaller in the meta-model in other regions, especially on the western Louisiana Shelf where POM deposition is small but where bottom water temperatures and O_2 concentrations are elevated. NH_4 flux is also much higher in the meta-model in regions of high POM deposition and somewhat higher where hypoxia occurs (Fig. S2). In the other areas NH_4 flux is 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.

Some of the discrepancies between model and observations can 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 key driver of diagenetic processes is POM deposition. However, observations of POM deposition are not available. Using POM deposition climatologies from a biogeochemical model as we have done here is thus a source of uncertainty. This is demonstrated by the improved agreement between simulated and observed sediment–water fluxes when including POM deposition in the optimization.

Since the meta-model parameterization requires steady state forcing, the diagenetic model was used at steady state for both the optimization of the parameter set and the meta-model parameterization for consistency. Using time-varying forcing for the optimization would not have changed the results significantly given the constraint of the dataset on the optimization.

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.

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 and Rosenberg, 1995; Middelburg and Levin, 2009). This result is also consistent the dominance of bacteria over inverte-

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brates 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 rate of the fast decaying organic matter pool ($R_2(T)$). The optimum temperature of remineralization (T_{opt}), the remineralization rate 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 three meta-models 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. The re-

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sulting meta-models exhibit realistic dynamics such as the increase of sediment–water fluxes in regions of high POM deposition, the decrease of 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 flat relationship between O_2 flux and bottom O_2 concentration in hypoxic conditions; in the meta-model, ODU is the dominant source of O_2 consumption in hypoxic conditions and at high POM depositional flux ($F_{POM} > 5\,\mathrm{mmol\,N\,m^{-2}\,d^{-1}}$), 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 with decreasing bottom O_2 in the hypoxic range. However, Lehrter et al. (2012) found an increase of the DIC/O_2 flux ratio with bottom O_2 depletion that they attributed to the production of reduced substances that accumulate in the sediment, diffuse back and reoxidize in the water column when O_2 becomes available. This 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) an Laurent and Fennel (2014).

The meta-models simulate 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

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(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 level 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. Here we presented a method to compute meta-models of sediment–water fluxes in regional biogeochemical models 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

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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 bottom water concentrations and sediment–water fluxes 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, R. C.: The effects of macrobenthos on chemical properties of marine sediment and overlying water, in: Animal-Sediment Relations, Plenum Press, New York, 53–102, 1982.

Boudreau, B. P.: Diagenetic Models and Their Implementation: Modelling Transport and Reactions in Aquatic Sediments, Springer, Berlin, 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, 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., 93, 17–26, doi:10.1016/j.csr.2014.11.005, 2014.

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.

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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., 33, 245–303, 1995.

DiToro, D. M.: Sediment Flux Modeling, Wiley and Sons, New York, 2001.

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, 1028–1042, doi:10.1016/j.ecolmodel.2009.04.054, 2010.

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. Cy., 20, 1–14, 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, 159–178, doi:10.1007/s10533-008-9270-z, 2009.

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.-Oceans, 118, 990–1002, doi:10.1002/jgrc.20077, 2013.

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, 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, 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. Marine Syst., 70, 49–62, doi:10.1016/j.jmarsys.2007.03.002, 2008.

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, 1545–1563, doi:10.4319/lo.1990.35.7.1545, 1990.

Laurent, A. and Fennel, K.: Simulated reduction of hypoxia in the northern Gulf of Mexico due to phosphorus limitation, Elementa, 2, 000022, doi:10.12952/journal.elementa.000022, 2014.

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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, 1861–1872, doi:10.1016/j.csr.2009.07.001, 2009.

Lehrter, J. C., Beddick Jr., D. L., Devereux, R., Yates, D. F., and Murrell, M. C.: 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. Ac., 38, 703–714, 1974.

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: Liu, K.-K., Atkinson, L., Quiñones, R. A., and Talaue-McManus, L., Springer, Berlin, 3–24, 2010.

Meysman, F. J. R., Middelburg, J. J., Herman, P. M. J., and Heip, C. H. R.: Reactive transport in surface sediments. I. Model complexity and software quality, Comput. Geosci., 29, 291–300, doi:10.1016/S0098-3004(03)00006-2, 2003a.

Meysman, F. J. R., Middelburg, J. J., Herman, P. M. J., and Heip, C. H. R.: Reactive transport in surface sediments. II. Media: an object-oriented problem-solving environment for early diagenesis, Comput. Geosci., 29, 301–318, doi:10.1016/S0098-3004(03)00007-4, 2003b.

Middelburg, J. J. and Levin, L. A.: Coastal hypoxia and sediment biogeochemistry, Biogeosciences, 6, 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, edited by: Brink, K. H. and Robinson, A. R., vol. 13, John Wiley and Sons, New York, 353–373, 2005.

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

Morse, J. W. and Berner, R. A.: What determines sedimentary C/S ratios?, Geochim. Cosmochim. Ac., 59, 1073–1077, 1995.

Mulsow, S., Boudreau, B. P., and Smith, J. A.: Bioturbation and porosity gradients, Limnol. Oceanogr., 43, 1–9, 1998.

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Murrell, M. C. and Lehrter, J. C.: Sediment and lower water column oxygen consumption in the seasonally hypoxic region of the Louisiana continental shelf, Estuar. Coast., 34, 912–924, 2011.
Murrell, M. C., Aukamp, J. R., Beddick, D. L., Devereux, R., Greene, R. M., Hagy, J. D., Jarvis, B. M., Kurtz, J. C., Lehrter, J. C., and Yates, D. F.: Gulf of Mexico hypoxia research program data report: 2002–2007, U.S. Environmental Protection Agency, Washington, DC, EPA/600/R-13/257, 2013.
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, 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. Coastal 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, 39–63, doi:10.1023/A:1020388503274, 2002.
Rabouille, C. and Gaillard, J.-F.: Towards the EDGE: Early diagenetic global explanation. A model depicting the early diagenesis of organic matter, O_2, NO_3, Mn, and PO_4, Geochim. Cosmochim. Ac., 55, 2511–2525, doi:10.1016/0016-7037(91)90369-G, 1991.
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. Ac., 65, 3615–3641, 2001.
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, 1097–1106, 2002.
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, 225–246, doi:10.1007/BF00008583, 1995.
Soetaert, K., Herman, P. M. J., and Middelburg, J. J.: A model of early diagenetic processes from the shelf to abyssal depths, Geochim. Cosmochim. Ac., 60, 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. Oceanogr., 41, 1651–1668, 1996b.

Soetaert, K., Middelburg, J. J., Herman, P. M. J., and Buis, K.: On the coupling of benthic and pelagic biogeochemical models, Earth Sci. Rev., 51, 173–201, 2000.

Wilson, R. F., Fennel, K., and Mattern, P. 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.

Wollast, R.: Evaluation and comparison of the global carbon cycle in the coastal zone and in the open ocean, in: The Global Coastal Ocean. Processes and Methods, edited by: Brink, K. H. and Robinson, A. R., vol. 10, John Wiley and Sons, New York, 213–252, 1998.

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. Soil Sediment., 14, 218–229, doi:10.1007/s11368-013-0793-0, 2013.

Xu, J. and Hood, R. R.: Modeling biogeochemical cycles in Chesapeake Bay with a coupled physical–biological model, Estuar. Coast. Shelf S., 69, 19–46, doi:10.1016/j.ecss.2006.03.021, 2006.

Yu, L., Fennel, K., Laurent, A., Murrell, M. C., and Lehrter, J. C.: Numerical analysis of the primary processes controlling oxygen dynamics on the Louisiana shelf, Biogeosciences, 12, 2063–2076, doi:10.5194/bg-12-2063-2015, 2015.

Table 1. Bottom water conditions at stations Z02 and Z03 in 2006. These data are used to optimize the diagenetic model. POM deposition flux (F_{POM}) was not measured; F_{POM} monthly climatologies were calculated for station Z02 and Z03 from a multiyear simulation with a biogeochemical circulation model (see Sect. 2.3).

Station	Date	F_{POM} mmol N m^{-2} d^{-1}	Salinity	Temperature °C	NO_3 mmol m^{-3}	NH_4 mmol m^{-3}	O_2 mmol m^{-3}
Z02	Apr	3.53	33.0	21.6	7.16	0.58	60.2
	Jun	2.19	36.0	24.0	8.61	7.93	0.0
	Sep	0.95	35.4	29.6	8.45	0.32	16.0
Z03	Apr	1.36	36.2	21.7	1.50	0.47	67.9
	Jun	1.20	35.9	25.7	1.90	2.40	137.9
	Sep	0.44	35.1	29.1	5.63	0.82	118.4

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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
	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	cmy^{-1}
D_{NH_4}	*	0.847		Diffusion coefficient for ammonium at 0 °C	$cm^2\,d^{-1}$
D_{NO_3}	*	0.845		Diffusion coefficient for nitrate at 0 °C	$cm^2\,d^{-1}$
D_{O_2}	*	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_{NH_4}	*	0.0336		T-dependent coefficient for ammonium diffusion	y^{-1}
a_{NO_3}	*	0.0303		T-dependent coefficient for nitrate diffusion	y^{-1}
a_{O_2}	*	0.0386		T-dependent coefficient for oxygen diffusion	y^{-1}
a_{ODU}	*	0.0242		T-dependent coefficient for ODU diffusion	y^{-1}
z_{bio}	1.0	5.0	(+)	Depth of bioturbated layer	cm
$Dbio_0$	8.784	1.53	(+)	Bioturbation "diffusivity"	$cm^2\,y^{-1}$
Db_{coeff}	*	1.0		Exponential decay below bioturbated layer	
$R_1^{T_{opt}}$	0.0213	0.02	(+)	Remineralization rate at T_{opt} for slow decaying OM1 pool	yr^{-1}
r_{om1}	0.10	0.13		N : C ratio for the OM1 pool	
$R_2^{T_{opt}}$	2.821	2.0	(+)	Remineralization rate at T_{opt} for fast decaying OM2 pool	yr^{-1}
r_{om2}	*	0.15		N : C ratio for the OM2 pool	
PB	0.00	0.05	(+)	Permanent burial of ODUs	
k_{O_2}	20.0	3.0	(+)	Half-saturation, O_2 limitation on aerobic remineralization	$\mu mol\,O_2\,L^{-1}$
kin_{odu}	0.1	5.0	(+)	Half-saturation, O_2 inhibition on anaerobic remineralization	$\mu mol\,O_2\,L^{-1}$
ox_{odu}	11.45	20.0	(+)	Maximum oxidation rate of ODUs	day^{-1}
k_{odu}	20.0	1.0	(+)	Half-saturation, O_2 in ODU oxidation	$\mu mol\,O_2\,L^{-1}$
Nit	50.0	20.0	(+)	Maximum nitrification rate	day^{-1}
k_{nit}	0.1	1.0	(+)	Half-saturation, O_2 inhibition on nitrification	$\mu mol\,O_2\,L^{-1}$
k_{dnf}	1.0	30.0	(+)	Half-saturation, nitrate limitation of denitrification	$\mu mol\,NO_3\,L^{-1}$
kin_{dnf}	30.0	10.0	(+)	O_2 inhibition of denitrification	$\mu mol\,O_2\,L^{-1}$
kin_{anox}	0.1	5.0	(+)	Half-saturation, nitrate inhibition of anaerobic remin.	$\mu mol\,NO_3\,m^{-3}$
oc_{frac2}	*	0.74		Fraction of deposited organic carbon into OM2 pool	
θ_{r1}	3.0	–	(+)	Q_{10} parameter for r_1	
θ_{r2}	3.0	–	(+)	Q_{10} parameter for r_2	
θ_{bio}	2.0	–	(+)	Q_{10} parameter for the bioturbation of solids	
T_{opt}	30.0	–	(+)	Optimum temperature for Q_{10} relationship	°C
α_0	0.0002	–	(+)	Non-local mixing coefficient	yr^{-1}

Table 3. Cost of each variable type at station Z02 and Z03 calculated using Eq. (3). 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	Z02	0.6	0.2	0.0	–	0.8
	Z03	5.4	2.9	68.5	–	76.8
$+F_{POM}$	Total	6.0	3.1	68.5	–	77.6

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Table 4. Meta-model coefficients for sediment O_2 consumption (SOC), 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 contribution of each input variable is indicated as well as the direction of its effect. The contributions were calculated from standardized coefficients. Bold values indicate the two dominant variables for each meta-model.

		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}
F_{O_2}	x_i	−17.6054	−3.5657	−1.5442	4.1427	−0.2751	−0.0376	−0.0273
	x_i^2		−0.0441	0.0671	−0.1596	−0.0369	0.0022	0.0001
	x_i^3		0.0007	−0.0009	0.0017	0.0022	−0.0000	−0.0000
	Contribution (%)		**79.7**	2.5	**10.3**	3.5	0.7	3.3
	Effect direction		−	−	−	−	+	−
F_{NH_4}	x_i	−2.9753	0.0356	0.2646	0.2272	−0.1077	0.0106	−0.0367
	x_i^2		0.0288	−0.0079	−0.0132	0.0373	−0.0002	0.0002
	x_i^3		−0.0004	0.0001	0.0002	−0.0016	0.0000	−0.0000
	Contribution (%)		**65.4**	8.3	9.5	4.2	1.4	**11.2**
	Effect direction		+	+	+	+	+	−
F_{NO_3}	x_i	2.2111	0.0387	0.0023	−0.3662	0.1024	−0.0160	0.0162
	x_i^2		−0.0022	−0.0003	0.0151	−0.0181	0.0000	−0.0001
	x_i^3		0.0000	0.0000	−0.0002	0.0006	−0.0000	0.0000
	Contribution (%)		0.0	4.9	22.0	4.2	**39.3**	**29.6**
	Effect direction		−	−	−	+	−	+

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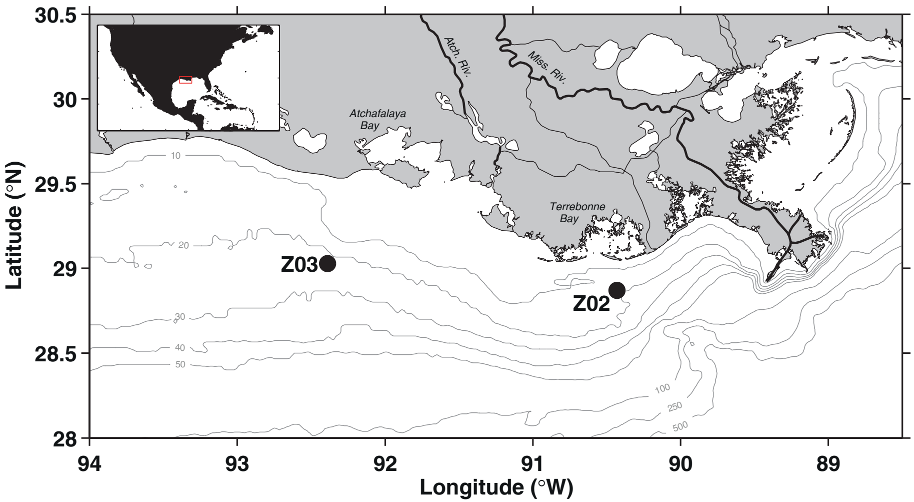

Figure 1. Map of the Louisiana Shelf showing the location of sample collection sites Z02 and Z03.

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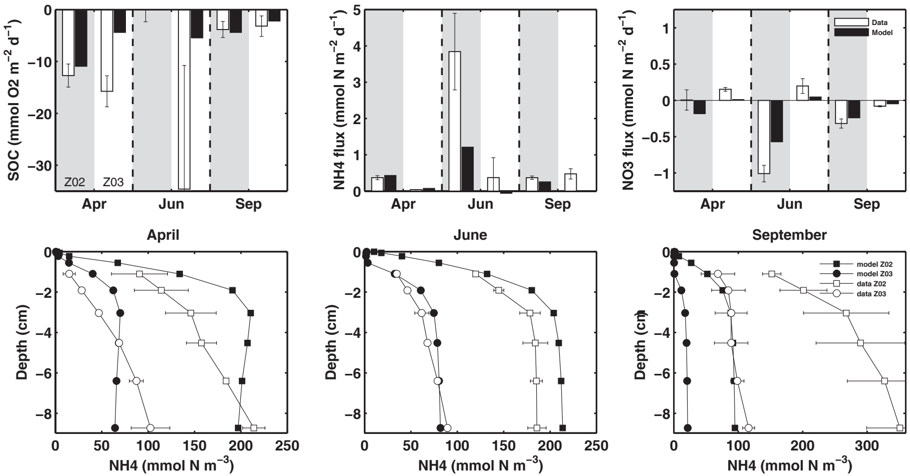

Figure 2. Model-data comparison of sediment water fluxes (top row) and NH_4 profiles (bottom row) for sites Z02 and Z03. Simulations use the optimized parameter set (baseline).

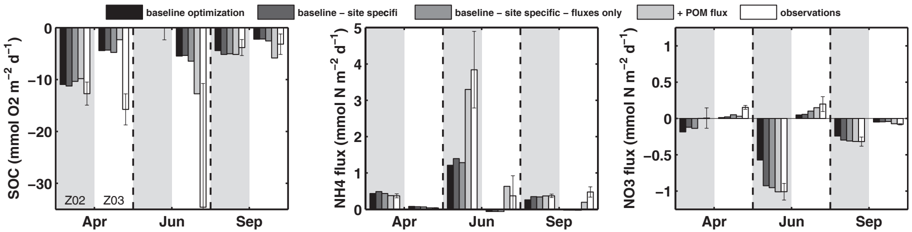

Figure 3. Model-data comparison of sediment water fluxes at stations Z02 and Z03 for several different optimization schemes (baseline includes all constraints).

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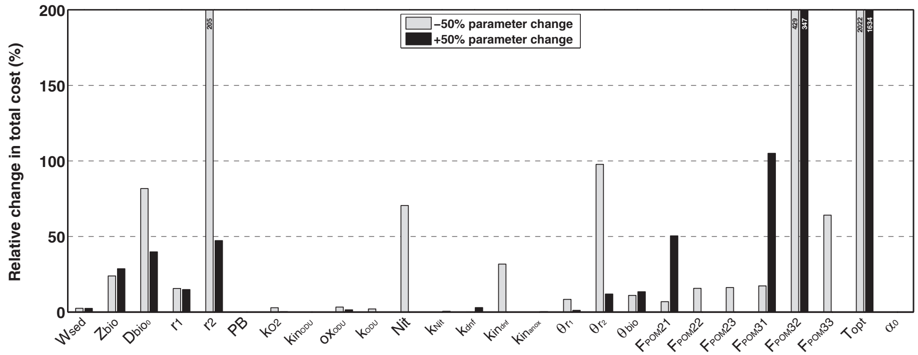

Figure 4. Sensitivity of model results to parameter variation.

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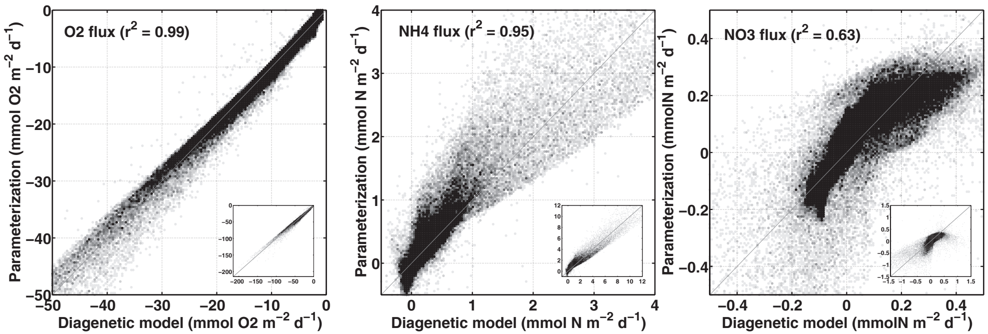

Figure 5. Comparison of sediment–water fluxes simulated with the diagenetic model (*x* axis) and predicted with the meta-model (*y* axis). Inset panels show the full range of data points, while main panels zoom in to the majority of data points for clarity.

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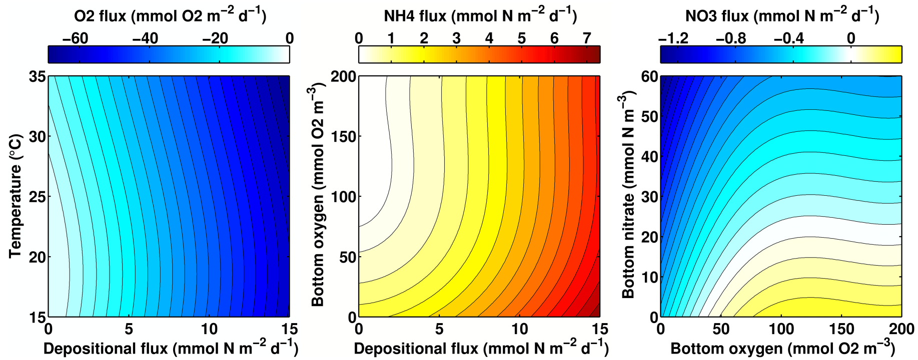

Figure 6. Influence of the two main contributors to O_2, NH_4 and NO_3 fluxes. Negative fluxes (blue shades) are into the sediment and positive fluxes (orange shades) are out of the sediment.

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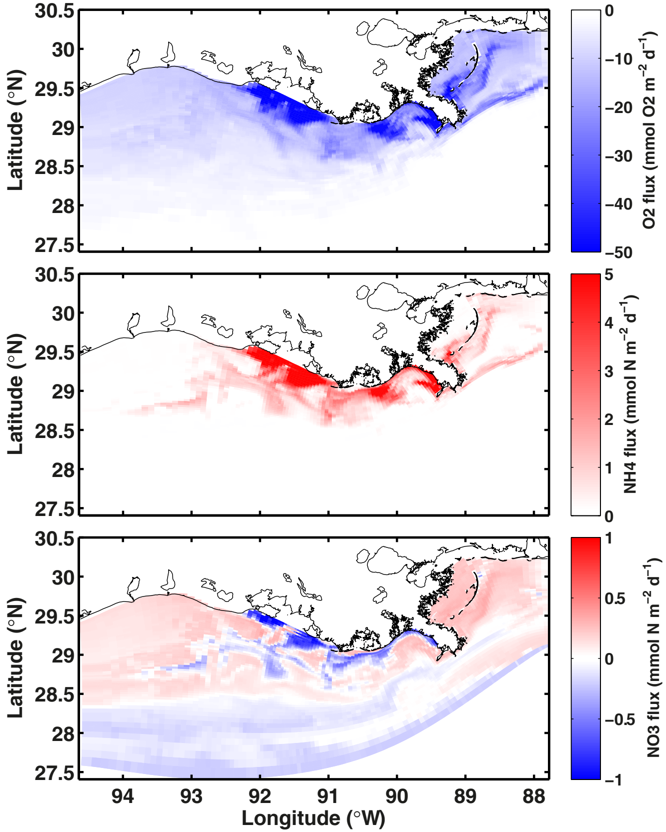

Figure 7. Spatial distribution of parameterized O_2, NH_4 and NO_3 fluxes during the LUMCON cruise in July 2009. Negative fluxes (blue) are into the sediment.

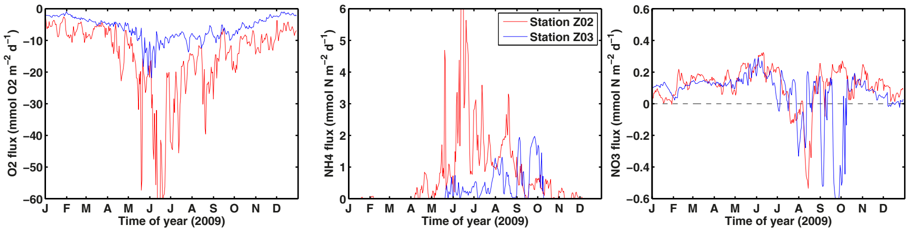

Figure 8. Temporal variability of parameterized O_2, NH_4 and NO_3 fluxes at station Z02 and Z03 in 2009. Negative fluxes are into the sediment.

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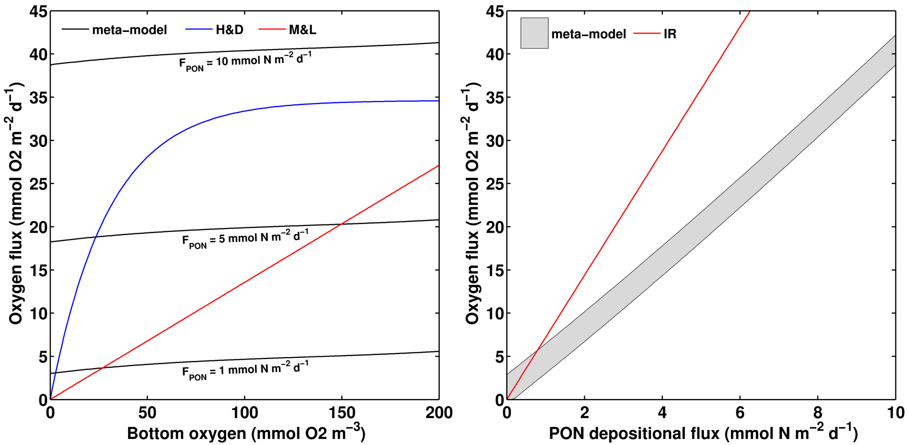

Figure 9. O_2 flux in the meta-model compared to that from the IR, H&D and M&L parameterizations as a function of bottom O_2 concentration (left) and of POM depositional flux (right). The grey area on the right panel corresponds to the variation in O_2 flux when bottom O_2 concentration range from 0 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).

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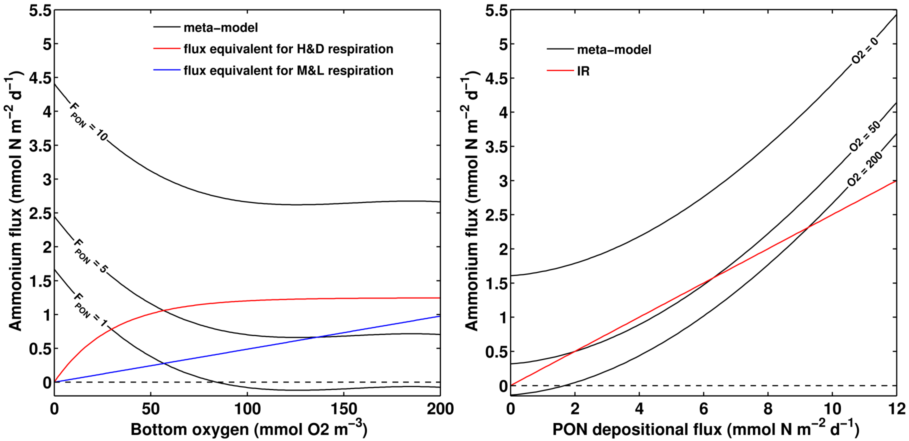

Figure 10. NH_4 flux in the meta-model compared with that from the IR, H&D and M&L parameterizations. NH_4 flux is represented as a function of (left) bottom O_2 concentration and (right) PON depositional flux.