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


Arnaud Laurent[1], Katja Fennel[1], Robin Wilson[1], John Lehrter[2] and Richard Devereux[2]

[1]Department of oceanography, Dalhousie University, Halifax, Canada. [2]US EPA Gulf Ecology Division, Gulf Breeze, USA . Correspondence to A. Laurent (arnaud.laurent@dal.ca)





## Abstract

Sediment biogeochemical processes are important drivers of water column biogeochemistry in coastal areas. For example, sediment oxygen consumption can be an important driver of bottom water oxygen depletion in hypoxic systems, and sediment-water nutrient fluxes support primary productivity in the overlying water column. Yet, biogeochemical sediment-water fluxes are often parameterized crudely and only poorly constrained in coupled physical-biogeochemical models. Here, we present a method for parameterizing biogeochemical sediment-water fluxes realistically and efficiently, using in-situ measurements and a steady state diagenetic model. We apply this method to the Louisiana Shelf where high primary production, induced by excess nutrient loads from the Mississippi-Atchafalaya River system, promotes the development of hypoxic bottom waters in summer. The parameterizations result in realistic sediment O2 consumption and sediment-water NH4 and NO3 fluxes on the Louisiana Shelf. The parameterized sediment-water fluxes enable a feedback between water column and sediment processes at low bottom oxygen concentrations, which is important for hypoxic systems such as the Louisiana Shelf.


## Methods

Biogeochemical sediment-water fluxes are parameterized using a diagenetic model in three successive steps. First, the parameter set of the diagenetic model is optimized for the Louisiana Shelf using in-situ measurements of sediment-water fluxes and sediment profiles. The optimized model is run in various configurations and a multiple regression model is constructed for each sediment-water flux (O2, NH4 and NO3).

### 1. Diagenetic model

The diagenetic model represents the dynamics of key solid and pore water constituents of the sediment involved in early diagenesis, as formulated by Soetaert et al. (1996). The model is vertically resolved and has 6 state variables: the solid volume of organic carbon (OC), split into a labile class (rapid remineralization) and a refractory class (slow remineralization), NO3, NH4, O2 and O2 demand units (ODU). Reduced substances produced by anoxic mineralization are added to the ODU pool rather than being explicitly modeled. Model processes include oxic mineralization, nitrification, denitrification, anoxic mineralization and ODU oxidation. The model is run at steady state to simulate sediment-water fluxes of pore water constituents, namely NO3, NH4, O2 and ODU.

### 2. Observations

We use observations from a series of cruises carried out on the Louisiana Shelf in April, June and September 2006. The stations visited during the cruises are grouped into two groups: a Zone 2 group located on the eastern Louisiana Shelf and influenced by the Mississippi River delta and a Zone 3 group further downstream on the western Louisiana Shelf (Fig. 1). The dataset includes sediment O2 consumption (SOC) and sediment-water fluxes of NH4 and NO3 (Lehrter et al, 2011) and sediment profiles of NH4 (Devereux et al, 2014).

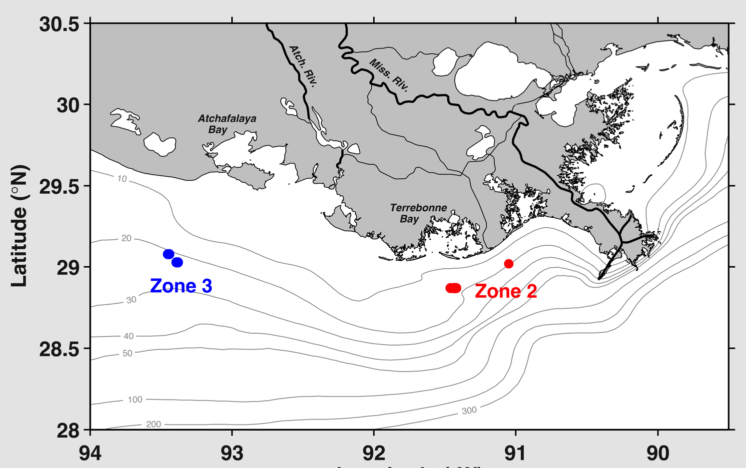


Figure 1. Louisiana Shelf bathymetry (grey contours; m) and locations of Zone 2 and Zone 3 stations.

### 3. Parameter optimization

The diagenetic model has 29 parameters (Tab. 1). Sediment porosity parameters were chosen to obtain a porosity profile within the observed range. Given the lack of observations on the labile and refractory fraction of OC and on their C:N ratio, their values were set following Wilson et al. (2013). The exponential decay coefficient for bioturbation was set as in the original model (Soetaert et al. 1996). These parameters were excluded from the optimization. The values of the remaining 21 parameters were optimized to best describe the observed sediment profiles and sediment-water fluxes. The parameter set is optimized using an evolution algorithm. This stochastic technique was successfully used with diagenetic models (Wilson et al. 2013; Wood et al. 2013). The evolution algorithm mimics natural selection by selecting the "fittest" set of parameters to reproduce the observations, through random recombinations and "mutations" of parameters over N generations. At each generations, the diagenetic model is run at steady state in 6 configurations, i.e. for each station/time where observations are available, and the model results compared to observations using a cost function to determine the fitness of each parameter set. During the optimization, the diagenetic model is forced with bottom water conditions observed during each cruise (Lehrter et al 2011). Depositional flux was not available to force the model and therefore this variable was included in the optimization.

Table 1. Optimized diagenetic model parameter set.

| Symbol | Value | Parameter description | Units |
|---|---|---|---|
| $H$ | 10 | Active sediment depth | cm |
| $\Phi_0$ | 0.95 | Porosity at surface | |
| $\Phi_{inf}$ | 0. 50 | Porosity at depth H | |
| $\Phi_{coef}$ | 4.0 | Porosity decay coefficient | $cm^{-1}$ |
| $w_{sed}$ | 0. 05 | Burial velocity | $cm\ y^{-1}$ |
| $D$ | 3.37 | Diffusion coefficient | $cm^2\ d^{-1}$ |
| $z_{bio}$ | 1.48 | Depth of bioturbated layer | cm |
| $Dbio_0$ | 20.8 | Bioturbation "diffusivity" | $cm^2\ y^{-1}$ |
| $Db_{coeff}$ | 1.0 | Exponential decay coefficient | $cm^{-1}$ |
| $r_1$ | 0.005 | Remin. rate, slow decaying OM1 pool | $yr^{-1}$ |
| $r_{om1}$ | 0.10 | mol N:mol C for OM1 | |
| $r_2$ | 2.6 | Rem. rate, fast decaying OM2 pool | $yr^{-1}$ |
| $r_{om2}$ | 0.15 | mol N:mol C for OM2 | |
| $PB$ | 0.00 | Permanent burial of ODUs | |
| $ko2$ | 20 | Half-sat, O2 limitation on aerobic remin. | $\mu molO_2\ L^{-1}$ |
| $kin_{odu}$ | 0.1 | Half-sat, O2 inhibition on anaerobic. remin. | $\mu molO_2\ L^{-1}$ |
| $ox_{odu}$ | 6.8 | Max oxidation rate of ODUs | $day^{-1}$ |
| $k_{odu}$ | 20 | Half-sat, O2 in ODU oxidation | $\mu molO_2\ L^{-1}$ |
| $Nit$ | 50 | Maximum nitrification rate | $day^{-1}$ |
| $k_{nit}$ | 0.1 | Half-sat, O2 inhibition on nitrification | $\mu molO_2\ L^{-1}$ |
| $k_{dnf}$ | 1.72 | Half-sat, NO3 limitation of denitrification | $\mu molNO_3\ L^{-1}$ |
| $kin_{dnf}$ | 26.4 | O2 inhibition of denitrification | $\mu molO_2\ L^{-1}$ |
| $kin_{anox}$ | 0.8 | Half-sat, NO3 inhibition of anaerobic remin. | $\mu molNO_3\ m^{-3}$ |
| $oc_{frac2}$ | 0.74 | Fraction of deposited OC into OM2 pool | |
| $\vartheta_{r1}$ | 1.50 | T-dependancy of $r_1$ | |
| $\vartheta_{r2}$ | 1.50 | T-dependancy of $r_2$ | |
| $\vartheta_{Dpw}$ | 1.00 | T-dependancy of Dpw | |
| $\vartheta_{Ds}$ | 1.50 | T-dependancy of Ds | |
| $T_{opt}$ | 21.25 | Optimum temperature | °C |

### 4. Meta-modelling

Meta-modelling was used to parameterize SOC and sediment-water flux of NH4 (FNH4) and NO3 (FNO3). This technique combines the simplicity and efficiency of a bottom water parameterization based on empirical or simple mass-conservation relationships with the realism of a diagenetic model. The diagenetic model was run at steady state using the optimized parameter set and forced with an extensive set of bottom water conditions randomly selected from the model results of Fennel et al (2013). A total of 10,000 model runs were carried out. A regression model was then calculated to relate each sediment-water flux $y$ with the $n$ bottom water variables $x_i$ such that:

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

## Results

### 1. Parameter optimization

The optimized parameter set is presented in Tab. 1 and model results using the optimized parameter set are compared with observations in Fig. 2. Overall, the agreement between model results and observations improves significantly with the optimized parameter set. The magnitude and direction of the fluxes are well resolved by the model (Fig 2a-f). Modeled O2 flux is split into SOC and ODU flux whereas only SOC is measured (Fig 2a,b). The magnitude of O2 fluxes is reasonable although the model tend to underestimate observed SOC in spring.

Observed NH4 and NO3 fluxes are very well resolved by the model (Fig. 2c-f). The model resolves both the spatial and temporal variability in nutrient fluxes on the Louisiana Shelf. Large nutrient fluxes occur in Zone 2 near the Mississippi delta during the productive season (Fig. 2c,e). Hypoxia occurs at this time and bottom waters become a source of NO3 to the sediment (Fig 2e). The magnitude of nutrient fluxes decrease significantly in Zone 3 on the western Louisiana Shelf (Fig. 2d,f). The optimized diagenetic model is able to simulate these characteristics of the system. Sediment NH4 concentrations are also represented reasonably well (Fig. 2g,h). The model simulates large NH4 sediment concentrations in Zone 2 (Fig. 2g) and small concentrations in Zone 3 (Fig. 2 h) which agrees with observations. The main discrepancy occurs in September when the model underestimates observed NH4 concentrations.

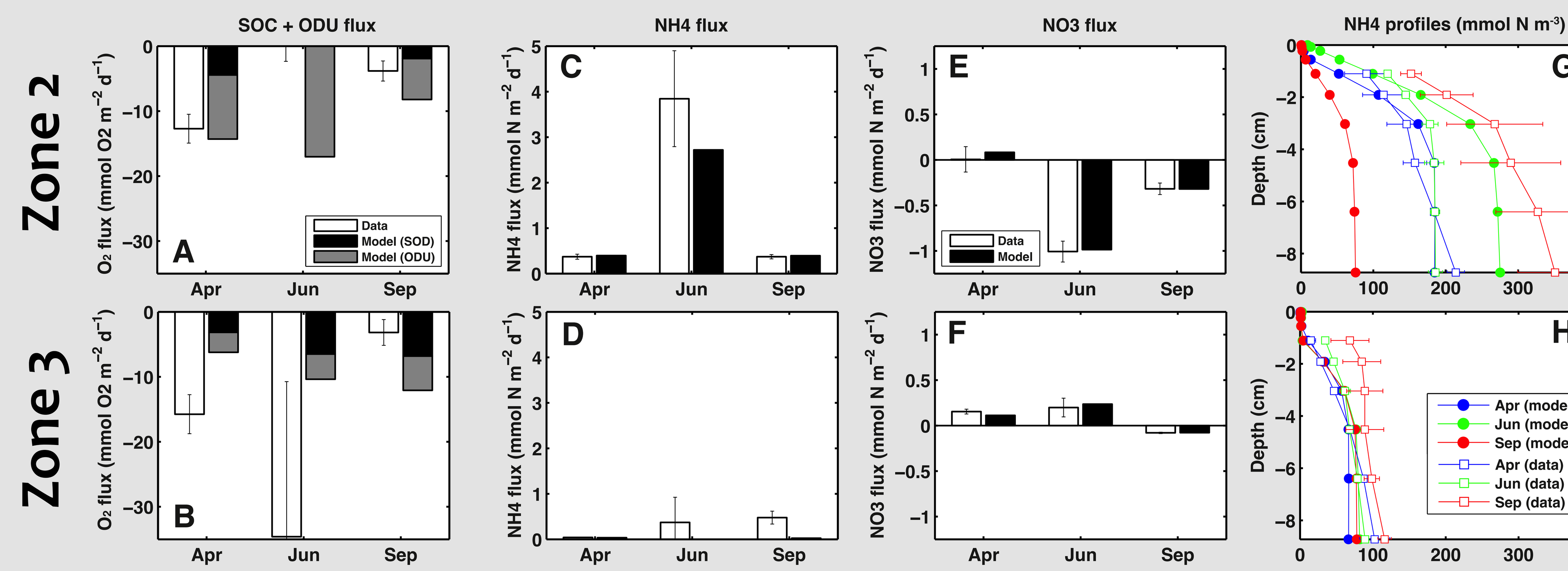


Figure 2. Comparison of observed and simulated SOC (A-B), sediment-water fluxes of NH4 (C-D) and NO3 (E-F), and sediment NH4 concentrations (G-H) at Zone 2 (upper panels) and Zone 3 (lower panels) stations in April, June and September 2006. Error bars indicate the standard deviation of the observations.

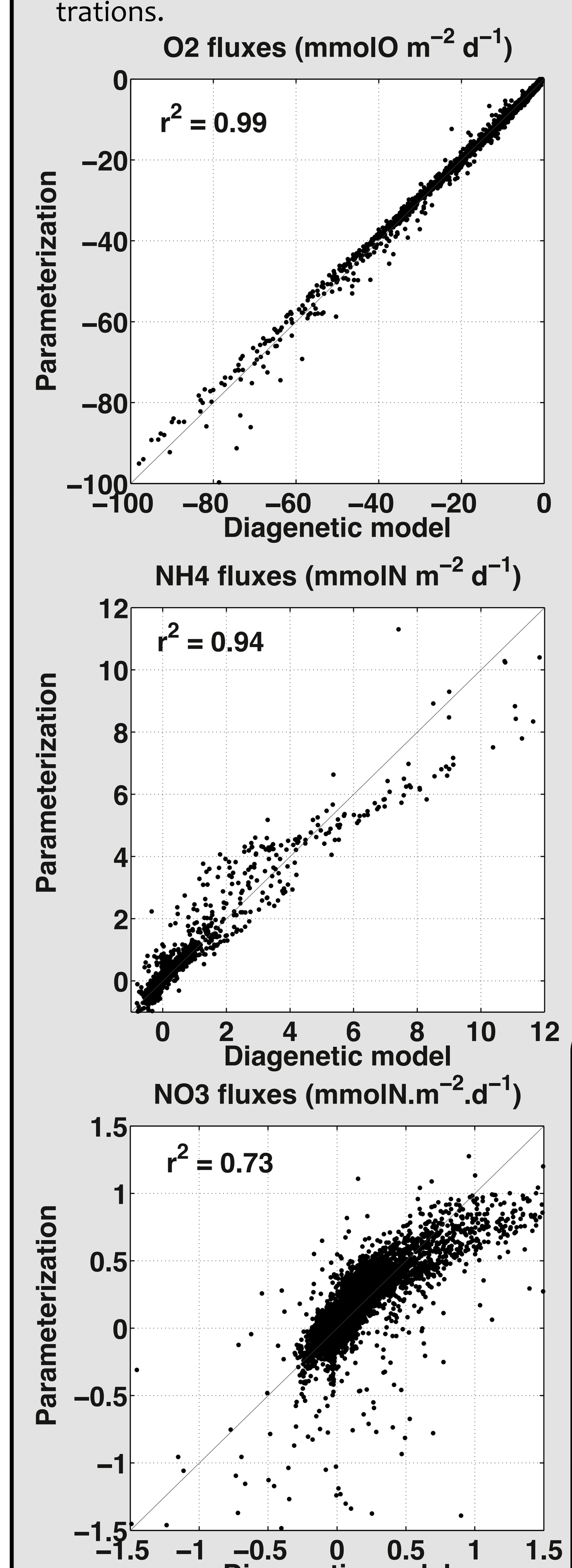


Figure 3. Sediment-water fluxes simulated with the diagenetic model (x-axis) versus the parameterization with the regression models (y-axis).

### 2. Sediment-water flux parameterization

The meta-model parameterizations (i.e. regression models, Eq. 1) predict well sediment-water fluxes simulated with the diagenetic model (Fig. 3). The comparison between modeled and parameterized fluxes is very good for O2 ($r^2$ = 0.99) and NH4 ($r^2$ = 0.94) fluxes. NO3 fluxes are also well predicted by the meta-model ($r^2$ = 0.73). The lower predictive skill of the NO3 flux parameterization is due to a more complex relationship; all the predictive variables influence the resulting NO3 flux, whereas SOC and NH4 flux are mostly driven by 2-3 variables (Tab. 2). The overall good agreement between the diagenetic model and the meta-model indicates that sediment-water fluxes can be approximated with relatively simple parameterizations. This is an important result which implies that a fully coupled diagenetic model may not be necessary to simulate realistically sediment-water fluxes in a coupled circulation-biogeochemical model.

Table 2. Standardized meta-model coefficients for sediment O2 consumption (SOC), NH4 flux (FNH4) and NO3 flux (FNO3). Coefficients refer to the general relationship presented in Eq. 1. Dashes indicate the absence of a cubic term for that variable. We arbitrarily define the significance of a coefficient in the regression model when its absolute value is above 0.3 (indicated in bold).

| | | $F_{POC}$ (mmol N $m^{-2}$ $d^{-1}$) | Salinity | Temperature (°C) | $NH_4$ (mmol $m^{-3}$) | $NO_3$ (mmol $m^{-3}$) | $O_2$ (mmol $m^{-3}$) |
|---|---|---|---|---|---|---|---|
| SOC | $b_i$ | **−1.0416** | −0.1237 | **1.0549** | −0.0182 | 0.0300 | **−0.4450** |
| | $c_i$ | 0.0554 | 0.1148 | **−2.0891** | 0.0281 | −0.0240 | **1.0199** |
| | $d_i$ | - | - | **0.9853** | - | - | **−0.5965** |
| $F_{NH4}$ | $b_i$ | 0.1160 | **0.9628** | **0.5453** | −0.2065 | 0.0852 | **−3.6840** |
| | $c_i$ | **0.6823** | **−0.8454** | **−1.0675** | 0.1948 | 0.0098 | **7.0276** |
| | $d_i$ | - | - | **0.5357** | - | - | **−3.5605** |
| $F_{NO3}$ | $b_i$ | **0.8350** | **−1.4977** | **−11.4111** | **0.3916** | **−0.4744** | **5.5479** |
| | $c_i$ | **−0.6744** | **1.3705** | **21.4632** | **−0.3769** | −0.2087 | **−11.5939** |
| | $d_i$ | - | - | **−10.4356** | - | - | **6.3920** |

The standardized coefficients of each parameterization are given in Tab 2. These coefficients indicate the weight of each predictive variable in the regression model and their sign the direction of the control. We find that SOC is controlled by deposition flux, temperature and bottom O2 concentration. Similarly, NH4 flux is controlled by deposition flux, temperature, O2 concentration and salinity, whereas all explanatory variables exert a control over NO3 flux (Tab. 2). The effect of the two dominant predictors on each flux is presented in Fig. 4. SOC is dominated by depositional flux and increases (i.e. more negative) above 25°C (Fig. 4a). NH4 flux is also driven by depositional flux but its magnitude is controlled by bottom O2 conditions (Fig. 4b). Under oxic conditions (O2 > 62.5 mmol O2 $m^{-3}$), NH4 flux from the sediment increases linearly with increasing depositional flux but remain relatively small due to nitrification in the sediment. When bottom waters are hypoxic (O2 < 62.5 mmol O2 $m^{-3}$), coupled nitrification-denitrification diminishes and more NH4 is returned to the water column, resulting in larger NH4 flux for a given depositional flux. The two main drivers of NO3 flux are bottom O2 concentration and temperature (Fig. 4c). NO3 flux varies almost linearly with bottom O2 but the direction of the flux depends on oxic or hypoxic conditions. In oxic conditions, a nearly constant efflux occurs. However, at low O2, bottom water NO3 becomes a source to the sediment, indicating the occurrence of direct denitrification in the sediment. The parameterizations are thus able to simulate the O2-dependent positive feedback between eutrophication and denitrification (Kemp et al 1990). This is an important feature for eutrophicated systems such as the Northern Gulf of Mexico.

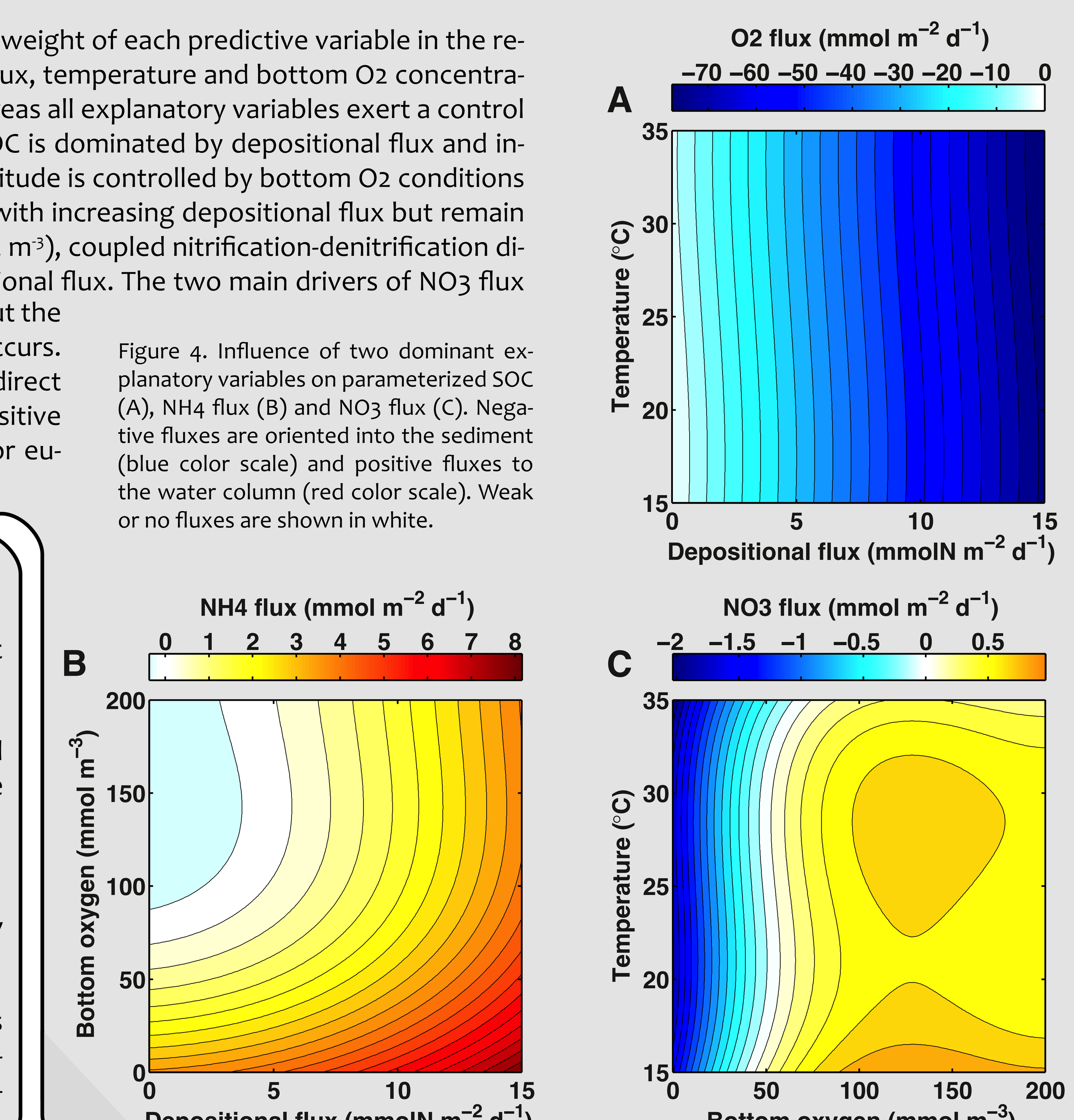


Figure 4. Influence of two dominant explanatory variables on parameterized SOC (A), NH4 flux (B) and NO3 flux (C). Negative fluxes are oriented into the sediment (blue color scale) and positive fluxes to the water column (red color scale). Weak or no fluxes are shown in white.

## Conclusions

We successfully used a meta-model technique to parameterize sediment-water fluxes using a diagenetic model optimized for the Louisiana Shelf region. Our results show that:

- The evolutionary algorithm method is able to optimize the parameter set to simulate the temporal and spatial variability in sediment-water fluxes and sediment NH4 concentration observed on the Louisiana Shelf
- The meta-model technique is effective and results in realistic sediment-water fluxes
- Simple sediment-water flux meta-model parameterizations can be effective replacements to a fully coupled diagenetic model

This method can be used in other coastal and shelf environments, in particular in eutrophicated systems such as the Louisiana Shelf. Our next step is to incorporate the meta-model parameterizations in a coupled circulation-biogeochemical model of the Louisiana Shelf and test the effect on water column biogeochemistry and hypoxia.

## Bibliography


Devereux et al (submitted). Manganese, Iron, and sulfur cycling in Louisiana continental shelf sediments.

Fennel et al (2011). A coupled physical-biological model of the Northern Gulf of Mexico shelf: model description, validation and analysis of phytoplankton variability. Biogeosciences, 8(7), 1881–1899.

Kemp et al (1990). Ammonium recycling versus denitrification Chesapeake Bay sediments. Limnology and Oceanography 35, 1545-1563.

Lehrter et al (2011). Sediment-water fluxes of dissolved inorganic carbon, O2, nutrients, and N2 from the hypoxic region of the Louisiana continental shelf. Biogeochemistry, 109(1-3), 233–252.

Soetaert et al (1996). A model of early diagenetic processes from the shelf to ahyssal depths. Geochimica et Cosmochimica Acta, 60(6), 1019–1040.

Wilson et al (2013). Simulating sediment–water exchange of nutrients and oxygen: A comparative assessment of models against mesocosm observations. Continental Shelf Research, 63, 69–84.

Wood et al (2013). Modelling macronutrients in shelf sea sediments: fitting model output to experimental data using a genetic algorithm. Journal of Soils and Sediments, 14(1), 218–229.


Link to poster