Supplementary Material

Strong and dynamic benthic-pelagic coupling and feedbacks in a coastal upwelling system (Peruvian shelf)

Andrew W. Dale[1*], Michelle Graco[2], Klaus Wallmann[1]

[1] GEOMAR Helmholtz Centre for Ocean Research Kiel, Kiel, Germany

[2] Instituto del Mar del Perú (IMARPE), Callao, Perú

* Correspondence:
Dr. Andrew Dale
adale@geomar.de

1   Non-steady state model

The model is based on the non-steady state version developed previously (Dale et al., 2016) and is designed to represent shelf sediments on the Peruvian margin. Model parametrization is based on the simulations in the earlier study. It considers 9 solutes including nitrate stored inside vacuolated sulfide oxidizing bacteria and particulate organic carbon (POC). A full list of reactions used in the model is provided in Table S1. Table S2 lists the stoichiometry for production/consumption of each biogeochemical variable. Model parameters are given in Table S3 and upper boundary conditions in Table S4.

The following mass conservation equation was used to describe the change in concentration of solutes and solids (C) in time and space for the steady state model (Berner, 1980; Boudreau, 1997; Berg, 2003):

$$\left(\xi\varphi+\kappa(1-\varphi)\right)\frac{\partial C}{\partial t}=\frac{\partial\left(\left(\varphi\xi(D_S+D_B)+\kappa(1-\varphi)D_B\right)\frac{\partial C}{\partial x}\right)}{\partial x}-\frac{\partial\left((\xi\varphi v_d+\kappa(1-\varphi)v_s)C\right)}{\partial x}$$
$$+\left(\xi\varphi+\kappa(1-\varphi)\right)\sum R \tag{S1}$$

with $\xi = 1, \kappa = 0$ if C is a solute

$\xi = 0, \kappa = 1$ if C is a solid

Solute and solid concentrations were modeled in units of mmol cm^{-3} of porewater and dry weight percent (wt.%), respectively. In Eq. (S1), t (yr) is time, x (cm) is depth below the sediment–water interface, φ (dimensionless) is porosity, v_d (cm yr^{-1}) is the burial velocity for dissolved species, v_s (cm yr^{-1}) is the burial velocity for solids, D_S (cm^2 yr^{-1}) is the tortuosity-corrected molecular diffusion coefficient, and D_B (cm² yr^{-1}) is the bioturbation coefficient. ΣR is the sum of concentration changes due to chemical reactions. The implementation of intracellular nitrate is explained below.

Porosity was described using an exponential function assuming steady–state compaction:

$$\varphi = \varphi(L) + (\varphi(0) - \varphi(L)) \exp\left(-\frac{x}{z_{por}}\right) \tag{S2}$$

where $\varphi(0)$ is the porosity at the sediment–water interface, $\varphi(L)$ is the porosity below the depth of compaction and z_{por} (cm) is the porosity depth attenuation coefficient.

Sediment compaction was considered by allowing the sediment burial velocity to decrease with sediment depth. The burial velocities of solids ($v_s(x)$) and solutes ($v_d(x)$) were then described as:

$$v_S(x) = \frac{\omega_{acc} \cdot (1 - \varphi(L))}{1 - \varphi(x)} \tag{S3}$$

$$v_d(x) = \frac{\omega_{acc} \cdot \varphi(L)}{\varphi(x)} \tag{S4}$$

In these equations, ω_{acc} corresponds to the burial velocity of compacted sediments (Table S3).

Solute–specific diffusion coefficients in sediments were calculated from the temperature–dependent molecular diffusion coefficients in seawater (D_{SW}) and corrected for tortuosity using the modified Weissberg equation (θ^2) (Boudreau, 1997; Schulz, 2000):

$$D_S = \frac{D_{SW}}{\theta^2} = \frac{D_{SW}}{1 - 2\ln(\varphi)} \tag{S5}$$

The decrease in bioturbation intensity with depth was described as (Boudreau, 1996):

$$D_B = D_B(0) \exp\left(-\frac{x^2}{2\,x_s^2}\right) \tag{S6}$$

where $D_B(0)$ (cm^2 yr^{-1}) is the bioturbation coefficient at the sediment–water interface and x_s (cm) is the bioturbation halving depth, both constrained by modeling excess ^{210}Pb data (Dale et al., 2015).

The modeled reaction network and rate expressions are summarized from Bohlen et al. (2011), as is the numbering of the reactions in the present model. The degradation of POC forms the basis of the biogeochemical cycling in the model. POC is linked to organic nitrogen via the atomic N:C ratio, r_{NC}, such that POC mineralization simultaneously produces DIC and NH_4^+. POC was degraded by aerobic respiration (R_1), denitrification (R_2, R_3), and sulfate reduction (R_5). Metal oxide reduction was not considered since it makes a minor contribution to carbon respiration, and methanogenesis is not included because sulfate does not become exhausted in the upper 50 cm (Dale et al., 2016). The relative rates of each POC degradation pathway were determined using Michaelis–Menten kinetics whereby the electron acceptors were used sequentially as defined by their respective half saturation constants (e.g. Boudreau, 1997). Each POC degradation pathway is dependent on electron acceptor concentrations, but the total bulk POC degradation rate is not. The rate of POC degradation was constrained using a multi-G approach as described in the main manuscript and in further detail below. DIC is produced by POC degradation only, that is, carbonate dissolution and precipitation was not considered since these processes amount to < 5% of benthic DIC fluxes (Dale et al., 2015).

The modeled N cycle is described in the manuscript. Biological NO_3^- transport by *Thioploca* ('BNO_3^-', where B stands for 'biological') was modeled explicitly as a non-local source term as described by Dale et al. (2016). The equation describing the transport and reduction of BNO_3^- by DNRA is:

$$\frac{\partial BNO_3^-}{\partial t} = \alpha_{B,0}\exp\left(-\frac{x^2}{2\,x_B^2}\right)(BNO_3^-{}^* - BNO_3^-) + R_9 \tag{S7}$$

where $\alpha_{B,0}$ (yr^{-1}) is the coefficient for biological NO_3^- transport at the sediment surface, x_B is the depth where over which the microbial mat density diminishes by 50%, and R_9 is the rate of DNRA (Table S1). The term $BNO_3^-{}^*$ in Eq. (S7) is equivalent to the upper boundary concentration of intracellular nitrate (on a total volume basis) and varies proportionally to

NO_3^-. Best results were found by assuming that BNO_3^-* is 300 times the boundary NO_3^- concentration, which agrees with field measurements of total intracellular nitrate inventories made at 12 °S (Dale et al., 2016). As shown by Dale et al. (2016), this allows a sedimentary BNO_3^- pool to exist even though the oceanic nitrate reservoir may become depleted. The coefficient x_B arbitrarily set to 1 cm to reflect the fact that thick *Thioploca* mats occupy the upper 2 cm of sediment, whilst recognizing that individual filaments extend much deeper into the sediment (Dale et al., 2016).

Upper boundary conditions are described in the main manuscript and in Table S4. At the lower boundary ($x = L$), all species were prescribed a zero–gradient (Neumann) condition. The set of partial differential equations was solved over a variable spatial grid with >700 nodes increasing from ~10 μm at the surface to 1 mm at depth using the numerical solver NDSolve in Mathematica 10. Mass conservation was better than 99.99%.

2 Derivation of POC kinetics and fluxes using a multi-G model

The model was also used to determine the parameters of the multi-G model (step 3 in Section 3.1 in the main manuscript) by fitting the multi-G model against the mean RPOC and POC profiles for the OMZ stations (step 2). This version requires only POC as a variable since the total degradation of POC is independent of other chemical species. For each of the 4 POC fractions, i, the following equation was solved:

$$\left(1-\varphi\right)\frac{\partial POC_i}{\partial t} = \frac{\partial\left(\left(1-\varphi\right)D_B\frac{\partial POC_i}{\partial x}\right)}{\partial x} - \frac{\partial\left(\left(1-\varphi\right)v_s POC_i\right)}{\partial x} - \left(1-\varphi\right)k_{Gi}\cdot POC_i \tag{S8}$$

The final term on the right hand side represents POC degradation. The model was applied in steady-state model, that is, where the term on the left-hand side equals zero. In the main manuscript (Section 3.1), we comment on the uncertainty introduced by this assumption It is necessary to solve these equations using a numerical rather than analytical approach since the porosity and bioturbation are functions of sediment depth, x. The upper boundary of each POC pool was assigned a constant flux, equal to a fraction of the total rain rate (17 mmol m^{-2} d^{-1} or 204 mg m^{-2} d^{-1}). Lower boundary conditions were set to a zero gradient condition (Neumann boundary). The sediment accumulation rate (0.15 cm yr^{-1}) and bioturbation coefficient (2 cm^2 yr^{-1}) were taken as the average values for the OMZ stations (Dale et al., 2015). The fluxes and rate constants, k_{Gi}, of each fraction were optimized against the mean

RPOC and POC profiles. Optimization against only one of these would be insufficient, since the rate of POC degradation is a function of its rate constant and POC content. As an initial constraint of the reactivities, k_{G1} and k_{G2} were set 8 yr^{-1} and 0.8 yr^{-1}, respectively, on the basis of degradation experiments of fresh phytodetritus under anoxic conditions (see main manuscript). These values allow a fine constraint on the RPOC and POC profiles in the upper few centimeters where almost half of the total POC is degraded (See Fig. 2 and Table 1 in the main manuscript). This may be partly fortuitous, since the best-fit rate constants and fluxes are unique for the imposed sediment accumulation rate and bioturbation coefficient. However, the order of magnitude is certainly correct, which to some extent provides empirical support for our modeled POC degradation.

References

Berg, P., Rysgaard, S., and Thamdrup, B. (2003) Dynamic modeling of early diagenesis and nutrient cycling. A case study in an Arctic marine sediment. *Am. J. Sci.* 303, 905-955.

Berner, R. A. Early Diagenesis: A Theoretical Approach. Princeton University Press, Princeton, 241 pp. 1980.

Bohlen, L., Dale, A. W., Sommer, S., Mosch, T., Hensen, C., Noffke, A., Scholz, F., Wallmann, K. (2011) Benthic nitrogen cycling traversing the Peruvian oxygen minimum zone. *Geochim. Cosmochim. Acta* 75, 6094-6111.

Boudreau, B. P. (1997) *Diagenetic Models and Their Implementation: Modelling Transport and Reactions in Aquatic Sediments*, Springer-Verlag, Berlin, 414 pp.

Boudreau, B. P. (1996) A method-of-lines code for carbon and nutrient diagenesis in aquatic sediments. *Comput. Geosci.* 22, 479-496.

Dale, A. W., Sommer, S., Lomnitz, U., Montes, I., Treude, T., Liebetrau, V., Gier, J. , Hensen, C., Dengler, M., Stolpovsky, K., Bryant, L. D., & Wallmann, K. (2015) Organic carbon production, mineralisation and preservation on the Peruvian margin. Biogeosciences 12, 1537-1559.

Dale A. W., Sommer S., Lomnitz U., Bourbonnais A. and Wallmann K. (2016) Biological nitrate transport in sediments on the Peruvian margin mitigates benthic sulfide emissions and drives pelagic N loss during stagnation events. *Deep-Sea. Res. I* 112, 123–136.

Schulz, H. D. (2000) Conceptual models and computer models. In H. D. Schulz, M. Zabel (eds) *Marine Geochemistry*, Springer-Verlag, Berlin, pp 417-442.

Table S1. Reaction network used in the non-steady state model. Numbering is based on Dale et al. (2016).

Stoichiometry	Rate expression [a]
R_1: $(CH_2O)(NH_3)_{rNC} + O_2 \rightarrow (1 - r_{NC})CO_2 +$ $r_{NC}\,HCO_3^- + r_{NC}\,NH_4^+ + (1 - r_{NC})H_2O$	$R_{POC} \cdot \dfrac{[O_2]}{[O_2] + K_1}$
R_2: $(CH_2O)(NH_3)_{rNC} + 2\,NO_3^- \rightarrow 2\,NO_2^- + (1 - rNC)\,CO_2 +$ $r_{NC}\,HCO_3^- + r_{NC}NH_4^+ + (1 - r_{NC})H_2O$	$R_{POC} \cdot \dfrac{[NO_3^-]}{[NO_3^-] + K_2} \cdot \dfrac{K_3}{[NO_2^-] + K_3} \cdot \dfrac{K_1}{[O_2] + K_1}$
R_3: $(CH_2O)(NH_3)_{rNC} + 4/3\,NO_2^- + (1/3 + rNC)CO_2 \rightarrow$ $2/3\,N_2 + (4/3 + r_{NC})HCO_3^- + r_{NC}NH_4^+ + (1/3 - r_{NC})H_2O$	$R_{POC} \cdot \dfrac{[NO_2^-]}{[NO_2^-] + K_3} \cdot \dfrac{K_1}{[O_2] + K_1}$
R_5: $(CH_2O)(NH_3)_{rNC} + 0.5\,SO_4^{2-} + r_{NC}CO_2 +$ $r_{NC}H_2O \rightarrow 0.5\,H_2S + (1 + r_{NC})HCO_3^- + r_{NC}NH_4^+$	$R_{POC} \cdot \dfrac{[SO_4^{2-}]}{[SO_4^{2-}] + K_4} \cdot \dfrac{K_2}{[NO_3^-] + K_2} \cdot \dfrac{K_3}{[NO_2^-] + K_3} \cdot \dfrac{K_1}{[O_2] + K_1}$
R_6: $NH_4^+ + 3/2\,O_2 + 2\,HCO_3^- \rightarrow NO_2^- + 3\,H_2O + 2\,CO_2$	$k_6 \cdot [O_2] \cdot [NH_4^+]$
R_7: $NO_2^- + 1/2\,O_2 \rightarrow NO_3^-$	$k_7 \cdot [O_2] \cdot [NO_2^-]$
R_8: $NH_4^+ + NO_2^- \rightarrow N_2 + 2\,H_2O$	$k_8 \cdot [NO_2^-] \cdot [NH_4^+]$
R_9: $HS^- + NO_3^- + CO_2 + 2\,H_2O \rightarrow SO_4^{2-} + NH_4^+ + HCO_3^-$	$k_9 \cdot \dfrac{[H_2S]}{[H_2S] + K_{DNRA}} \cdot [BNO_3^-]$
R_{13}: $HS^- + 2\,O_2 + HCO_3^- \rightarrow SO_4^{2-} + CO_2 + H_2O$	$k_{13} \cdot [O_2] \cdot [H_2S]$
R_{18}: $NO_3^- + 5/8H_2S \rightarrow 0.5N_2 + 5/8SO_4^{2-} + 0.5H_2O + 0.25H^+$	$k_{18} \cdot [NO_3^-] \cdot [H_2S]$
R_{19}: $NO_2^- + 3/8H_2S + 0.25H^+ \rightarrow 0.5N_2 + 3/8SO_4^{2-} + 0..5H_2O$	$k_{19} \cdot [NO_2^-] \cdot [H_2S]$

[a] The factor $f_i = \varphi/(1-\varphi) \cdot M_i/(10 \cdot ds)$ where M_i is the molecular mass of species i (g mol^{-1}), converts between dissolved species in units of mmol cm^{-3} of porewater and solid phase species in dry weight percent (wt.%).

Table S2. Rate expressions applied in the differential equations (ΣR in Eq. (S1)).

Variable	ΣR
O_2	$- R_1 - 3/2\ R_6 - 0.5\ R_7 - 2\ R_{13}$
NO_3^-	$- 2\ R_2 + R_7 - R_9 - R_{18}$
NO_2^-	$+ 2\ R_2 - 4/3\ R_3 + R_6 - R_8 - R_8 - R_{19}$
NH_4^+	$+ r_{NC}\ R_{POC} - R_6 - R_8 + R_9$
N_2	$+ 2/3\ R_3 + R_8 + 0.5R_{18} + 0.5R_{19}$
BNO_3^-	$- R_9$
SO_4^{2-}	$- 0.5\ R_4 + R_9 + R_{13} + 5/8R_{18} + 3/8R_{19}$
H_2S	$+ 0.5\ R_5 - R_8 - R_{13} - 5/8R_{18} - 3/8R_{19}$
TCO_2	$+ R_{POC}$
POC	$- R_{POC}$

Table S3. Model parameters. The parameter values are based on previous empirical model simulations for the Peruvian shelf (Dale et al., 2016) except for chemoautotrophic denitrification which is new to this study (see main manuscript).

Description	Value
Length of simulated sediment column, L (cm)	50
Bottom water temperature, T (K)	15
Dry sediment density, ρ (g cm^{-3})	2.5
Porosity at 0 cm, $\varphi(0)$ (–)	0.90
Porosity at L cm, $\varphi(L)$ (–)	0.80
Porosity attenuation length, z_{por} (cm)	0.1
Sediment burial velocity, ω_L (cm yr^{-1})	0.15
Bioturbation coefficient at sediment surface, $D_B(0)$ (cm^2 yr^{-1})	2
Bioturbation halving depth, x_s (cm)	2
Rate constant for aerobic oxidation of NH_4^+, k_6 (M^{-1} yr^{-1})	1×10^{10}
Rate constant for aerobic oxidation of NO_2^-, k_7 (M^{-1} yr^{-1})	1×10^{10}
Rate constant for anammox, k_8 (M^{-1} yr^{-1})	2×10^{9}
Rate constant for DNRA, k_9 (yr^{-1})	30
Rate constant for aerobic oxidation of H_2S, k_{13} (M^{-1} yr^{-1})	1×10^{11}
Rate constant for chemoautotrophic denitrification, k_{18} (M^{-1} yr^{-1})	1×10^{11}
Rate constant for chemoautotrophic denitrification, k_{19} (M^{-1} yr^{-1})	1×10^{11}
Half–saturation constant for O_2 for POC degradation, K_1 (μM)	2
Half–saturation constant for NO_3^- for POC degradation, K_2 (μM)	10
Half–saturation constant for NO_2^- for POC degradation, K_3 (μM)	1
Half–saturation constant for SO_4^{2-} for POC degradation, K_4 (μM)	50
Half–saturation constant for BNO_3^- for DNRA, K_{DNRA} (μM)	2
Atomic N–C ratio in deposited organic matter, r_{NC} (mol N / mol C)	16/106

Table S4. Boundary conditions at the sediment-water interface. Temporally variable concentrations are described in the main manuscript.

Description	Value
O_2 (μM)	variable
NO_3^- (μM)	variable
NO_2^- (μM)	variable
NH_4^+ (μM)	1×10^{-6}
N_2 (μM)	500
SO_4^{2-} (mM)	29
H_2S (μM)	0
TCO_2 (μM)	2171
BNO_3^- (μM)	variable
POC (mmol cm^{-2} yr^{-1})	variable