Modeling benthic–pelagic nutrient exchange processes and porewater distributions in a seasonally–hypoxic sediment: evidence for massive phosphate release by *Beggiatoa*?

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Supplementary Material

Parameters used in the biogeochemical model not listed in Table 3 are provided in Table A1. Boundary conditions are given in Table A2. Constitutive equations which define the transport terms, temperature corrections and conversion factors are given in Table A3. General details of these functions are presented in Dale et al. (2011).

The parameters for the porosity function were determined from the measured porosity values for all geochemical cores analyzed. Porosity was used, amongst others, to calculate in situ diffusion coefficients, D, from the molecular diffusion coefficients in porewater, D_W, for the bottom water temperature and mean salinity of 20 using data provided by Boudreau (1997) and Schulz (2006). D was therefore time dependent through the temperature.

The depth–dependent fluid velocity, $v_a(z)$, was calculated assuming steady state compaction (Berner, 1980). To account for the enhanced advection of dissolved CH_4 following gas eruption from the sediment, the upward velocity, $v_a(0,t)$, is subtracted from the downward movement of porewater due to burial. For all other solutes $v_a(0,t) = 0$.

Changes have been made with regard to the bioirrigation coefficient, α_{bi} (Eq. (1)), which was assumed to vary among solutes. This reasoning is based on previous observations by Aller (2001) and model simulations by Berg et al. (2003) and Meile et al. (2005) who showed that diffusion gradients across burrow walls can lead to unique irrigation coefficients for different species. The approach of Meile et al. (2005) is particularly insightful since they derived 1D irrigation coefficients from a virtual porewater data set generated using a 3D model which accounted for burrow geometry and reactions. They demonstrated that highly redox sensitive species such as Fe^{2+} tend to be oxidized on burrow walls, leading to zero apparent irrigation rates when analyzed using a 1D model (Meile et al., 2005). Similarly, owing to their reactivity, O_2 and TH_2S tend to be irrigated at about twice the rate of less reactive species such as SO_4^{2-}, NH_4^+ and TCO_2. Bioirrigation coefficients determined using the Br^- tracer experiment for an incubation length of around 7 days approximate those of SO_4^{2-}, TCO_2 and NH_4^+. This is because the radial concentration gradient of Br^- after this period displays vertical and radial concentration gradients around burrows characteristic of SO_4^{2-}, TCO_2 and NH_4^+. Therefore, in this study the coefficient γ_{bi} in Eq. (5a) was set equal to 1 for all solutes with the exception of O_2, TH_2S and Fe^{2+}, which were equal to 2 (for O_2 and TH_2S) and 0 (for Fe^{2+}).

The same first–order rate constant values for G1 ($k_{G1} = 1.4\times10^{-4}$ d^{-1}), G2 ($k_{G2} = 4.1\times10^{-6}$ d^{-1}) and G3 ($k_{G3} = 1.1\times10^{-6}$ d^{-1}) mineralization were used as in (Dale et al., 2011). k_{G1} was constrained using SR rates measured ex situ with $^{35}SO_4^{2-}$, whereas k_{G2} and k_{G3} were constrained using data from a gravity core taken at the same site. The reactivity of the G0 fraction representing fresh phytodetritus was set to 0.016 d^{-1} based on results by Graf et al. (1983) who determined that the spring bloom in Boknis Eck was consumed within 5–6 weeks of being deposited in the seabed. The data presented by Dale et al. (2011) correspond to the pre–spring bloom winter situation and consideration of this fraction was unnecessary in that study. Due to a lack of data, the N:C ratio of G0 was set to that of the G1 fraction (9.5/106) determined previously (Dale et al., 2011) which is close to the experimentally

determined composition of organic matter of 8.9/106 (Balzer et al., 1983). *(N:C)$_i$* for G1, G2 and G3 were unchanged from Dale et al. (2011). A Redfield P:C value of 1/106 estimated from porewater data and benthic chamber fluxes was prescribed for all carbon fractions (Balzer et al., 1983).

All reaction rate expressions include an additional term to allow for the widely–observed fact that biogeochemical reactions in marine sediments are sensitive to changes in temperature. All POM mineralization rate constants, with the exception of aerobic respiration and denitrification, were allowed to increase by a factor of 3 for every 10 ^{o}C increase in temperature, that is, using a Q_{10} value of 3 (Westrich and Berner, 1988; Klump and Martens, 1989). Aerobic respiration and denitrification were assigned a Q_{10} of 1.8 based on data presented by Thamdrup et al. (1998) and Rysgaard et al. (2004) for the temperature range characteristic of Boknis Eck bottom waters (0 to 10 ^{o}C). Anammox was better described with a Q_{10} of 2.5 since it responds more rapidly to rises in temperature over this range than denitrification (Dalsgaard and Thamdrup, 2002; Rysgaard et al., 2004). AOM was assigned a Q_{10} of 2 based on slurry incubations using sediment from the same site (Treude et al., 2005). Data on the temperature response of the other secondary redox reactions is, to our knowledge, not well established and these were assigned a Q_{10} of 2 (Fossing et al., 2004).

Table A1. Additional parameters used in the biogeochemical model.

Parameter	Description	Value	Unit	Main constraint
ρ_s	Dry sediment density	2.5	g cm^{-3}	Assumed (Dale et al., 2011)
$\varphi(0)$	Porosity at $z = 0$	0.94	1	Measured (this study) [a]
$\varphi(L)$	Porosity at $z = L$ (60 cm)	0.87	1	Measured (this study) [a]
z_{por}	Porosity attenuation length	1.25	cm	Measured (this study) [a]
$v_s(L)$	Sediment burial velocity	1.1×10^{-3}	cm d^{-1}	Excess ^{210}Pb (Nittrouer et al., 1998)
z_{bt}	Bioturbation attenuation coefficient	2	cm	Assumed based on steady state model (Dale et al., 2011)
Q_{10}	Temperature rate increase for POM mineralization	3.0	1	Experimentally determined (Westrich and Berner, 1988; Klump and Martens, 1989)
Q_{10}	Temperature rate increase for aerobic respiration and denitrification	1.8	1	Experimentally determined (Rysgaard et al., 2004; Thamdrup et al., 1988)
Q_{10}	Temperature rate increase for anammox	2.5	1	Experimentally determined (Rysgaard et al., 2004)
Q_{10}	Temperature rate increase for all other reactions	2	1	Assumed, based on Fossing et al. (2004)
T_{ref}	Reference temperature for reaction rates	2.1	^{o}C	Lowest temperature where SR was measured
k_{G0}	Rate constant for G0 degradation	0.016	d^{-1}	Protein content and ATP turnover (Graf et al., 1983)
k_{G1}	Rate constant for G1 degradation	1.4×10^{-4}	d^{-1}	Measured SR rates (Bertics et al., 2012)
k_{G2}	Rate constant for G2 degradation	4.1×10^{-6}	d^{-1}	Gravity core porewater data (Dale et al., 2011)
k_{G3}	Rate constant for G3 degradation	1.15×10^{-6}	d^{-1}	Gravity core porewater data (Dale et al., 2011)
f_{ox}	Enhancement factor for POM degradation by O_2	10	1	O_2 penetration depths from Preisler et al. (2007)
K_{O2}	Half–saturation constant for O_2	1	μM	Benthic fluxes and porewater modeling (Bohlen et al., 2011; Dale et al., 2011)
K_{NO3}	Half–saturation constant for NO_3^-	10	μM	Benthic fluxes and porewater modeling (Bohlen et al., 2011; Dale et al., 2011)
K_{NO2}	Half–saturation constant for NO_2^-	10	μM	Benthic fluxes and porewater modeling (Bohlen et al., 2011; Dale et al., 2011)
K_{Fe}	Half–saturation constant for Fe(OH)$_{3-A}$	0.028	wt–%	Benthic fluxes and porewater modeling (Bohlen et al., 2011; Dale et al., 2011)
K_{SO4}	Half–saturation constant for sulfate	0.5	mM	Flow through reactor experiments (Pallud and Van Cappellen, 2006)
K_{PO4}	Half–saturation constant for TPO$_4$ during R_{Fe2ox}	10	μM	Assumed (this study) [b]
k_{NH4ox}	Rate constant for aerobic oxidation of NH_4^+	2.7×10^4	M^{-1} d^{-1}	Benthic fluxes and porewater modeling (Bohlen et al., 2011; Dale et al., 2011)
k_{NO2ox}	Rate constant for aerobic oxidation of NO_2^-	2.7×10^4	M^{-1} d^{-1}	Benthic fluxes and porewater modeling (Bohlen et al., 2011; Dale et al., 2011)
k_{amx}	Rate constant for anammox	2.7×10^4	M^{-1} d^{-1}	Benthic fluxes and porewater modeling (Bohlen et al., 2011; Dale et al., 2011)
k_{DNRA}	Rate constant for DNRA	2.7×10^5	M^{-1} d^{-1}	Benthic fluxes and porewater modeling (Bohlen et al., 2011; Dale et al., 2011)
k_{H2Sox}	Rate constant for aerobic oxidation of TH$_2$S	2.7×10^4	M^{-1} d^{-1}	Benthic fluxes and porewater modeling (Bohlen et al., 2011; Dale et al., 2011)
k_{AOM}	Rate constant for AOM	0.27	d^{-1}	SO$_4^{2-}$ concentration profile (this study)
$(N{:}C)_0$	Molar mineralization ratio of N:C in G0	9.5/106	mol N (mol C)$^{-1}$	Assumed equal to $(N{:}C)_1$ and measured by Balzer et al. (1983)
$(N{:}C)_1$	Molar mineralization ratio of N:C in G1	9.5/106	mol N (mol C)$^{-1}$	Steady–state model (Dale et al., 2011)
$(N{:}C)_2$	Molar mineralization ratio of N:C in G2	8/106	mol N (mol C)$^{-1}$	Steady–state model (Dale et al., 2011)
$(N{:}C)_3$	Molar mineralization ratio of N:C in G3	27/106	mol N (mol C)$^{-1}$	Steady–state model (Dale et al., 2011)

[a] Mean porosity values from measurements in all multiple cores in Table 1.

[b] The TPO$_4$ concentration is relatively insensitive to this parameter, and is included to avoid negative TPO$_4$ concentrations (see main text).

Table A2: Boundary conditions used in the model. Time–dependent boundary conditions denoted 'variable' are shown in Fig. 1.

Variable	Value	Unit	Constraint
Upper solutes			
O_2	Variable	μM	Measured (Dale et al., 2011)
NO_3^-	6	μM	Measured (Dale et al., 2011)
$NO_{3\ bac}^-$	150	μM	Measured (Preisler et al., 2007)
NO_2^-	0.5	μM	Measured (Dale et al., 2011)
SO_4^{2-}	Variable	mM	Scaled to salinity (this study)
Fe^{2+}	0.1	μM	Assumed
NH_4^+	3	μM	Measured (Dale et al., 2011)
TPO_4	1.5	μM	Measured (this study)
CH_4	10	nM	Measured (Bange et al., 2010), assumed constant.
TCO_2	2	mM	Measured (this study)
TH_2S	0.1	μM	Measured (this study)
Br^-	Variable	mM	Scaled to salinity (this study)
Upper solids			
G0	Variable	$mmol\ m^{-2}\ d^{-1}$	POC flux (Balzer et al., 1986) minus G1, G2 and G3
G1	Variable	$mmol\ m^{-2}\ d^{-1}$	SR rates (this study)
G2	1.34	$mmol\ m^{-2}\ d^{-1}$	Gravity core porewater data (Dale et al., 2011)
G3	1.81	$mmol\ m^{-2}\ d^{-1}$	Gravity core porewater data (Dale et al., 2011)
$Fe(OH)_{3-A}$	0.41	$mmol\ m^{-2}\ d^{-1}$	[a]
$Fe(OH)_{3-B}$	0.41	$mmol\ m^{-2}\ d^{-1}$	[a]
$\Sigma Fe\text{-}P$	$0.82 \times \varepsilon$	$mmol\ m^{-2}\ d^{-1}$	[b]
FeS_2	0	$mmol\ m^{-2}\ d^{-1}$	Assumed
Lower solutes			
O_2	$\partial/\partial z = 0$	$mmol\ m^{-2}$	Assumed based on measured data
NO_3^-	$\partial/\partial z = 0$	$mmol\ m^{-2}$	Assumed based on measured data
NO_2^-	$\partial/\partial z = 0$	$mmol\ m^{-2}$	Assumed based on measured data
SO_4^{2-}	$\partial/\partial z = 0$	$mmol\ m^{-2}$	Assumed based on measured data
Fe^{2+}	$\partial/\partial z = 0$	$mmol\ m^{-2}$	Assumed based on measured data
NH_4^+	2500	μM	Assumed based on measured data
TPO_4	500	μM	Assumed based on measured data
CH_4	500	μM	Assumed based on model results (Dale et al., 2011)
TCO_2	30	mM	Assumed based on measured data
TH_2S	4000	μM	Assumed based on measured data
Br^-	$\partial/\partial z = 0$	$mmol\ m^{-2}$	Assumed based on measured data
Lower solids			
All solids	$\partial/\partial z = 0$	$mmol\ m^{-2}$	Assumed

[a] The total iron oxide flux is calculated from mass accumulation rates and iron concentrations (Balzer, 1982; Lapp and Balzer, 1993). The partitioning of the flux between the two pools is assumed to be equal.

[b] P:Fe molar ratio in iron oxyhydroxides (ε) based on model simulations by Slomp et al. (1996). Both $Fe(OH)_{3-A}$ and $Fe(OH)_{3-B}$ deposited on the seabed have an associated P fraction.

Table A3: Depth–dependent constitutive equations used in the biogeochemical model.

Parameter	Constitutive equation
Porosity	$\varphi(z) = \varphi(L) + (\varphi(0) - \varphi(L)) \cdot \exp\left(-\dfrac{z}{z_{por}}\right)$
Molecular diffusion in sediment [a]	$D(z,T) = \dfrac{D_{w}(T)}{1 - \ln(\varphi(z)^2)}$
Burial of solids	$v_s(z) = \dfrac{(1 - \varphi(L)) \cdot v_s(L)}{(1 - \varphi(z))}$
Burial of solutes [b]	$v_a(z,t) = \dfrac{v_s(L) \cdot \varphi(L) - v_a(0,t) \cdot \varphi(0)}{\varphi(z)}$
Bioturbation	$D_b(z,t) = D_b(0,t) \cdot \exp\left(-\dfrac{z^2}{2 \cdot z_{bt}^2}\right)$
Bioirrigation	$\alpha_{bl}(z,t) = \alpha_{bl1}(t) \cdot \dfrac{\exp(\alpha_{bl2}(t) - z)}{1 + \exp(\alpha_{bl2}(t) - z)}$
Intracellular nitrate transport	$\alpha_b(z,t) = \alpha_{b1}(t) \cdot \dfrac{\exp(\alpha_{b2} - z)}{1 + \exp(\alpha_{b2} - z)}$
Temperature correction for rates [a]	$f(T) = Q_{10}^{\left(\frac{T(t) - T_{ref}}{10}\right)}$
Conversion between solid (wt %) and dissolved species (mmol cm^{-3}) [c]	$f_X(z) = \dfrac{100\,\% \cdot M_W \cdot \varphi(z)}{10^3 \frac{\text{mmol}}{\text{mol}} \cdot \rho_s \cdot (1 - \varphi(z))}$

[a] Parameter depends on time through the temperature (T) dependency.
[b] Upward advection of solutes, $v_a(0,t)$, is used for CH_4 only. For all other species $v_a(0) = 0$.
[c] f_X where X = POC, Fe or P and M_W is the molecular weight in g mol^{-1}.

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