

DATA REPOSITORY ITEM 2009063

APPENDIX: MODEL SET-UP

The model, the Biogeochemical Reaction Network Simulator (BRNS, Regnier et al., 2003; Aguilera et al., 2005), is a simplified version of the one developed for Aarhus Bay sediments by Dale et al. (2008). The variables considered are SO_4^{2-} , $\text{CH}_{4(\text{aq})}$, $\text{CH}_{4(\text{g})}$ and particulate organic carbon (POC) concentrations. The reaction set is limited to sulfate reduction (R_1) coupled to POC mineralization, methanogenesis (R_2), AOM (R_3) and $\text{CH}_{4(\text{g})}$ dissolution (R_4) (Table A1). The vertical depth concentration and rate profiles in the 700 cm of Holocene mud are calculated by solving the one-dimensional mass conservation equations (Bernier, 1980; Boudreau, 1997) for solutes (Eq. A1a), solids (Eq. A1b) and $\text{CH}_{4(\text{g})}$ (Eq. A1c):

$$\varphi \frac{\partial C_S}{\partial t} = \frac{\partial}{\partial x} \left(\varphi (D_S + D_b) \frac{\partial C_S}{\partial x} \right) - \frac{\partial (\varphi v C_S)}{\partial x} + \varphi \alpha (C_{S,0} - C_S) + \varphi R_S \quad (\text{A1a})$$

$$(1-\varphi) \frac{\partial C_P}{\partial t} = \frac{\partial}{\partial x} \left((1-\varphi) D_b \frac{\partial C_P}{\partial x} \right) - \frac{\partial ((1-\varphi) v C_P)}{\partial x} + (1-\varphi) R_P \quad (\text{A1b})$$

$$\varphi \frac{\partial \text{CH}_{4(\text{g})}}{\partial t} = \frac{\partial}{\partial x} \left(\varphi D_{\text{CH}_{4(\text{g})}} \frac{\partial \text{CH}_{4(\text{g})}}{\partial x} \right) - \frac{\partial (\varphi v \text{CH}_{4(\text{g})})}{\partial x} + \varphi R_{\text{CH}_4} \quad (\text{A1c})$$

where x (cm) is the vertical depth below the sediment-water interface, t (y) is time, φ (L pore water (L wet sediment)⁻¹) is the depth-dependent porosity, C_S (mol L⁻¹) and C_P (mol g⁻¹) are the time-dependent concentrations of solutes and solids, respectively, $C_{S,0}$ (mol L⁻¹) and $\text{CH}_{4(\text{g}),0}$ (mol L⁻¹) are the solute and $\text{CH}_{4(\text{g})}$ concentration at the top of the core,

D_S ($\text{cm}^2 \text{y}^{-1}$) is the tortuosity-corrected molecular diffusion coefficient (Schulz, 2000), D_b ($\text{cm}^2 \text{y}^{-1}$) is the bioturbation coefficient, v (cm y^{-1}) is the sediment burial velocity, α (y^{-1}) is the bioirrigation coefficient and R is the sum of the rate of concentration change due to reactions. $D_{CH_4(g)}$ is an apparent diffusion coefficient for simulating $\text{CH}_4(g)$ transport (see below). As there is no evidence for externally-impressed flow due to groundwater seepage in Aarhus Bay, fluid advection was not considered. The model parameters and values are listed in Table A2, and are based on the earlier model for Aarhus Bay sediments (Dale et al., 2008).

The porosity of the sediment is assumed to decrease exponentially with depth due to steady-state compaction:

$$\varphi = \varphi_L + (\varphi_0 - \varphi_L) \exp(-x_{por} \cdot x) \quad (\text{A2})$$

where φ_0 and φ_L is the porosity at the sediment-water interface and at 700 cm, respectively, and x_{por} is the depth attenuation length of porosity.

Bioturbation, which acts on all model state variables, was quantified using the following formulation (Meile and Van Cappellen, 2005):

$$D_b = \frac{D_{b0}}{2} \operatorname{erfc}\left(\frac{x - x_{mix}}{x_T}\right) \quad (\text{A3})$$

where D_{b0} is the mixing intensity at the sediment-water interface, x_{mix} is the depth where D_b equals half of D_{b0} , and x_T is the characteristic depth scale over which the mixing decreases from full activity to zero.

Non-local pore water exchange through bioirrigation, α , at any depth, x , is calculated by:

$$\alpha = \alpha_0 \cdot \exp\left(\frac{x_1 - x}{x_2}\right) / \left(1 + \exp\left(\frac{x_1 - x}{x_2}\right)\right) \quad (\text{A4})$$

where α_0 is the bioirrigation intensity at the sediment-water interface, and x_1 and x_2 control the depth over which the exchange decreases from α_0 to zero.

Molecular diffusion coefficients were calculated according to Schulz (2000). Since no direct measurements were available to constrain the $\text{CH}_{4(\text{g})}$ transport rate, an apparent transport coefficient ($D_{\text{CH}_{4(\text{g})}}$) was used as a tuning parameter to simulate $\text{CH}_{4(\text{g})}$ transport. $\text{CH}_{4(\text{g})}$ transported upwards through the sediment was allowed to re-dissolve if the pore water was under-saturated with $\text{CH}_{4(\text{aq})}$, the saturation state being defined by the value of CH_4^{SOL} (mol L^{-1}). CH_4^{SOL} depends on salinity, temperature and pressure and was calculated from the fully-implicit iterative formulation of Duan et al. (1992). A constant salinity of 27 was used in the calculations, based on weekly time series data during 2004 which revealed a variation of 27 ± 2 in bottom water salinity with no seasonal pattern (Dale et al., 2008). The average bottom water temperature at the time of sampling was used in the calculation of CH_4^{SOL} (7.7 ± 0.2 °C, $n=19$). The variable water depth (i.e. hydrostatic pressure) over the bay has the largest effect on CH_4^{SOL} .

Numerical solution of the model required specification of the concentrations (solutes and $\text{CH}_{4(\text{g})}$) or fluxes (solids) at the sediment-water interface (Table A2). At the base of

the sediment, all model variables were prescribed with a zero-gradient (no flux) boundary condition, except for $\text{CH}_4(\text{g})$, which was fixed at 2.2 % gas volume (gas volume / total sediment volume). This gas fraction is similar to that used by Dale et al. (2008) to quantify gas phase dynamics in Aarhus Bay, and provides the main source of methane in the sediment.

In the sensitivity analyses, the following values were doubled from the values in Table A2 (i) the POC_{fast} and POC_{slow} fluxes to the sediment-water interface, F_{POC_i} (ii) the rate of POC_{fast} and POC_{slow} mineralization, k_i (iii) the intensity of bioturbation, D_{b0} , and (iv) the intensity of bioirrigation, α_0 .

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TABLE DR1. REACTIONS AND RATE EXPRESSIONS USED IN THE MODEL.

Reaction	Rate expression
$R_1: 2\text{CH}_2\text{O}_{(s)} + \text{SO}_4^{2-}{}_{(aq)} \rightarrow \Sigma\text{H}_2\text{S}_{(aq)} + \Sigma\text{CO}_2{}_{(aq)}$	$\Sigma k_i \text{POC}_i f_{\text{SO}_4}$
$R_2: 2\text{CH}_2\text{O}_{(s)} \rightarrow \text{CH}_4{}_{(aq)} + \Sigma\text{CO}_2{}_{(aq)}$	$\Sigma k_i \text{POC}_i (1 - SW_{\text{SO}_4}) (1 - f_{\text{SO}_4})$
	$f_{\text{SO}_4} = SW_{\text{SO}_4} + (1 - SW_{\text{SO}_4}) [\text{SO}_4^{2-}] / K_S$
	$SW_{\text{SO}_4} = \begin{cases} 1 & \text{if } [\text{SO}_4^{2-}] > K_S \\ 0 & \text{if } [\text{SO}_4^{2-}] < K_S \end{cases}$
$R_3: \text{CH}_4{}_{(aq)} + \text{SO}_4^{2-}{}_{(aq)} \rightarrow \Sigma\text{H}_2\text{S}_{(aq)} + \Sigma\text{CO}_2{}_{(aq)}$	$K_{AOM} \text{CH}_4{}_{(aq)} (\text{SO}_4^{2-}{}_{(aq)} / (\text{SO}_4^{2-}{}_{(aq)} + K_S))$
$R_4: \text{CH}_4{}_{(g)} \rightarrow \text{CH}_4{}_{(aq)}$	$k_{\text{diss}} (\text{CH}_4^{\text{SOL}} - \text{CH}_4{}_{(aq)}) \text{CH}_4{}_{(g)} (SW_{\text{CH}_4g})$
	$SW_{\text{CH}_4g} = \begin{cases} 1 & \text{if } \text{CH}_4{}_{(aq)} < \text{CH}_4^{\text{SOL}} \\ 0 & \text{if } \text{CH}_4{}_{(aq)} > \text{CH}_4^{\text{SOL}} \end{cases}$

Note: The rate expressions apply to carbon, and the POC fractions (POC_{*i*}) are assumed to be carbohydrate (CH₂O_(s)) for mass balance considerations. The total dissolved sulfide (ΣH₂S_(aq)) and dissolved inorganic carbon (ΣCO_{2(aq)}) reaction products are not modeled explicitly.

TABLE DR2. PARAMETERS AND BOUNDARY CONDITIONS USED IN THE MODEL.

Parameter	Description	Value	Unit
L	Length of model domain	700	cm
S	Salinity	27	—
T	Bottom water temperature	280.85	K
φ_0	Porosity at $x = 0$	0.80	—
φ_L	Porosity at $x = L$	0.70	—
x_{por}	Depth attenuation coefficient for porosity	0.02	cm^{-1}
v	Sediment accumulation rate	0.10	cm y^{-1}
α_0	Bioirrigation coefficient at $x=0$	19 *	y^{-1}
x_1	Attenuation coefficient 1 for bioirrigation	14.0	cm
x_2	Attenuation coefficient 2 for bioirrigation	1.0	cm
D_{b0}	Bioturbation intensity at $x=0$	12 *	$\text{cm}^2 \text{y}^{-1}$
x_{mix}	Halving depth of D_{b0}	15	cm
x_T	Mixing length scale due to bioturbation	5	cm
$D_{\text{SO}_4^{2-}}$	In situ diffusion coefficient for SO_4^{2-} at $x = 0$	198	$\text{cm}^2 \text{y}^{-1}$
D_{CH_4}	In situ diffusion coefficient for $\text{CH}_{4(\text{aq})}$ at $x = 0$	311	$\text{cm}^2 \text{y}^{-1}$
k_{fast}	Mineralization rate of POC_{fast}	0.1 *	y^{-1}
k_{slow}	Mineralization rate of POC_{slow}	0.001 *	y^{-1}
k_{AOM}	Rate constant for AOM	100	$\text{M}^{-1} \text{y}^{-1}$
k_{diss}	Rate constant for $\text{CH}_{4(\text{g})}$ dissolution	1000	$\text{M}^{-1} \text{y}^{-1}$
K_S	Rate-limiting constant for sulfate reduction	0.1	mM
$F_{\text{POC}_{fast}}$	Flux of POC_{fast} to the sediment	300 *	$\mu\text{mol cm}^{-2} \text{y}^{-1}$
$F_{\text{POC}_{slow}}$	Flux of POC_{slow} to the sediment	30 *	$\mu\text{mol cm}^{-2} \text{y}^{-1}$
$C_{0-\text{SO}_4^{2-}}$	SO_4^{2-} concentration at $x = 0$	22	mM
$C_{0-\text{CH}_4}$	$\text{CH}_{4(\text{aq})}$ concentration at $x = 0$	1.0	μM
$C_{0-\text{CH}_{4(\text{g})}}$	$\text{CH}_{4(\text{g})}$ concentration at $x = 0$	0.0	%
$C_{L-\text{CH}_{4(\text{g})}}$	Concentration of $\text{CH}_{4(\text{g})}$ at $x = L$	2.2	%
C_L	All other species at $x = L$	$\partial C/\partial x = 0$	—

* These values were doubled in the sensitivity analyses.