

# Effects of progressive oxygen depletion on sediment diagenesis and fluxes: A model for the lower St. Lawrence River Estuary

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Web Appendix 1. Model description, parameterization, and sensitivity analyses

## Description of the model

*Reactions and transport processes*—Our reaction-transport model (numerical code LSSE-Mega) solves a set of diagenetic equations (Berner 1980; Boudreau 1997) for the concentrations  $C_i(x,t)$  of solid (in mol per gram of dry weight) and dissolved (in mol  $\text{cm}^{-3}$ ) chemical species in the sediment:

$$\frac{\partial \varphi C_i}{\partial t} = \frac{\partial}{\partial x} \left( \varphi D_i \frac{\partial C_i}{\partial x} \right) - \frac{\partial}{\partial x} (\varphi U C_i) + \varphi \alpha_{\text{irr}} (C_i^0 - C_i^{\text{burr}}) + \sum_j \varphi v_{ij} R_j \quad (\text{A1.1a})$$

$$\frac{\partial \xi C_i}{\partial t} = \frac{\partial}{\partial x} \left( \xi D_b \frac{\partial C_i}{\partial x} \right) - \frac{\partial}{\partial x} (\xi U C_i) + \sum_j \xi v_{ij} R_j \quad (\text{A1.1b})$$

where Eq. A1.1a is for dissolved species, and Eq. A1.1b is for solid species. Here,  $t$  is time, and  $x$  is the depth coordinate below the sediment–water interface.  $U$  is the advection (burial) velocity.  $R_j$  values are the rates of chemical and biochemical reactions, and  $v_{ij}$  is the stoichiometric coefficient of species  $i$  in reaction  $j$ .  $\varphi$  is the sediment porosity. The factor  $\xi$  is equal to  $(1 - \varphi)\rho$ , where  $\rho$  is the density of dry sediment in  $\text{g cm}^{-3}$ . The effective diffusion coefficients  $D_i$  for solutes were calculated as sums of the bioturbation coefficient  $D_b$  and the appropriate molecular diffusion coefficients, which were corrected for sediment porosity using an Archie’s law factor of  $\varphi^{1.14}$  (Boudreau 1997), for salinity as described in Burdige (2006), and for temperature of  $T = 5^\circ\text{C}$  using expressions in Boudreau (1997). The rate constants for the rates  $R_j$  of chemical and biochemical reactions (Tables A1.1–A1.3) were taken from dSED, a database for modeling sediment diagenesis (Katsev et al. 2004). The coefficient  $\alpha_{\text{irr}}(x)$  describes bioirrigation,  $C_i^0$  is the dissolved substance concentration at the sediment–water interface, and  $C_i^{\text{burr}}$  is the concentration of that substance in a bioirrigated burrow (see following).

The boundary conditions at the sediment–water interface are imposed concentration (Dirichlet) for the dissolved species:

$$C_i(x = 0, t) = C_i^0(t) \quad (\text{A1.2})$$

and imposed flux (mixed-type) for the solid species:

$$-\xi D_i(0) \frac{\partial C_i}{\partial x} + \xi U C_i = F_i(t) \quad (\text{A1.3})$$

Here,  $F_i$  is the solid substance flux (in  $\text{mol cm}^{-2} \text{yr}^{-1}$ ) at the sediment–water interface. A no-gradient boundary condition is imposed for all species at the bottom of the integration domain ( $x = L$ ):

$$\partial C_i / \partial x|_{x=L} = 0 \quad (\text{A1.4})$$

Variation in the sediment porosity with depth was approximated to best fit the experimentally measured profiles of Mucci (2003, unpubl. data) and Silverberg et al. (1987) as  $\varphi(x) = 0.79 + (0.90 - 0.79) \exp(-0.25x)$ , where  $x$  is in cm. The depth dependence of the burial velocity was calculated from this porosity profile (Meysman et al. 2005) as

$$U(x) = U_L \varphi(L) / \varphi(x) \quad (\text{for solutes}) \quad (\text{A1.5a})$$

$$U(x) = U_L \xi(L) / \xi(x) \quad (\text{for solids}) \quad (\text{A1.5b})$$

where  $U_L$  is the burial velocity in the deep sediment (where it is the same for both the solid phases and pore water).

The decomposition of two different pools of sedimentary organic matter (reactive OM1 and refractory OM2) by the conventional sequence of electron acceptors (Froelich et al. 1979) was assumed to proceed according to Monod kinetics (Table A1.2). The inhibition constants,  $C_i^{\text{inh}}$ , characterize the oxidant concentrations above which the use of the less energetically favorable oxidants is inhibited (Boudreau 1997). For simplicity, they are assumed to be equal to the Monod half-saturation constants for the respective species,  $C_i^{\text{lim}}$ . The secondary redox reactions are assumed to be second order (first order with respect to the main reactants; Table A1.2) (Van Cappellen and Wang 1996). Mineral precipitation and dissolution rates are proportional to the respective super- or undersaturations (Table A1.2).

The pH-dependent adsorption of Mn(II) and Fe(II) ions onto solid sediment phases is described by equilibrium partitioning coefficients (Van Cappellen and Wang 1996) approximated by Langmuir isotherms:

$$K_{\text{adsFe}} = \sum_i \frac{K_{\text{Fe},i}^* X_i S_{\text{T}i}}{[H^+] + K_{\text{Fe},i}^* [\text{Fe}^{2+}] + K_{\text{Mn},i}^* [\text{Mn}^{2+}]} \quad (\text{A1.6})$$

$$K_{\text{adsMn}} = \sum_i \frac{K_{\text{Mn},i}^* X_i S_{\text{T}i}}{[H^+] + K_{\text{Fe},i}^* [\text{Fe}^{2+}] + K_{\text{Mn},i}^* [\text{Mn}^{2+}]} \quad (\text{A1.7})$$

Table A1.1. Reactions included in the model. S-X denotes a species X sorbed to a site S- on a solid substrate surface;  $R'$  are dissolution rates.

Kinetic reactions	Rates
<i>Primary redox reactions</i>	
$(\text{CH}_2\text{O})(\text{NH}_3)_y(\text{H}_3\text{PO}_4)_z + (1+2y)\text{O}_2 + y\text{HCO}_3^- \rightarrow (1+y)\text{CO}_2 + y\text{NO}_3^- + z\text{H}_3\text{PO}_4 + (1+y)\text{H}_2\text{O}$	$R_{\text{O}_2}$
$(\text{CH}_2\text{O})(\text{NH}_3)_y(\text{H}_3\text{PO}_4)_z + 4/5\text{NO}_3^- \rightarrow 1/5\text{CO}_2 + 4/5\text{HCO}_3^- + 2/5\text{N}_2 + y\text{NH}_3 + z\text{H}_3\text{PO}_4 + 3/5\text{H}_2\text{O}$	$R_{\text{NO}_3}$
$(\text{CH}_2\text{O})(\text{NH}_3)_y(\text{H}_3\text{PO}_4)_z + 2\text{MnO}_2 + (3+y)\text{CO}_2 + (1+y)\text{H}_2\text{O} \rightarrow 2\text{Mn}^{2+} + (4+y)\text{HCO}_3^- + y\text{NH}_4^+ + z\text{H}_3\text{PO}_4$	$R_{\text{MnO}_2}$
$(\text{CH}_2\text{O})(\text{NH}_3)_y(\text{H}_3\text{PO}_4)_z + 4\text{Fe}(\text{OH})_3 + 7\text{CO}_2 \rightarrow 4\text{Fe}^{2+} + 8\text{HCO}_3^- + y\text{NH}_3 + z\text{H}_3\text{PO}_4 + 3\text{H}_2\text{O}$	$R_{\text{Fe}(\text{OH})_3}$
$(\text{CH}_2\text{O})(\text{NH}_3)_y(\text{H}_3\text{PO}_4)_z + 1/2\text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + 1/2\text{H}_2\text{S} + y\text{NH}_3 + z\text{H}_3\text{PO}_4$	$R_{\text{SO}_4}$
$(\text{CH}_2\text{O})(\text{NH}_3)_y(\text{H}_3\text{PO}_4)_z \rightarrow 1/2\text{CH}_4 + 1/2\text{CO}_2 + y\text{NH}_3 + z\text{H}_3\text{PO}_4$	$R_{\text{CH}_4}$
<i>Secondary redox reactions</i>	
$4\text{Fe}^{2+} + \text{O}_2 + 8\text{HCO}_3^- + 2\text{H}_2\text{O} \rightarrow 4\text{Fe}(\text{OH})_3 + 8\text{CO}_2$	$R_{\text{FeOx}}$
$4\text{S-Fe}^+ + \text{O}_2 + 4\text{HCO}_3^- + 6\text{H}_2\text{O} \rightarrow 4\text{S-H}^0 + 4\text{Fe}(\text{OH})_3 + 4\text{CO}_2$	$R_{\text{surFe}}$
$\text{S-Mn}^+ + 1/2\text{O}_2 + \text{HCO}_3^- \rightarrow \text{S-H}^0 + \text{MnO}_2 + \text{CO}_2$	$R_{\text{surMn}}$
$\text{NH}_4^+ + 2\text{O}_2 + 2\text{HCO}_3^- \rightarrow \text{NO}_3^- + 2\text{CO}_2 + 3\text{H}_2\text{O}$	$R_{\text{NH}_4\text{Ox}}$
$\text{H}_2\text{S} + 2\text{O}_2 + 2\text{HCO}_3^- \rightarrow \text{SO}_4^{2-} + 2\text{CO}_2 + 2\text{H}_2\text{O}$	$R_{\text{SO}_x}$
$\text{FeS} + 2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{SO}_4^{2-}$	$R_{\text{FeSO}_x}$
$2\text{FeS}_2 + 9\text{O}_2 + 5\text{H}_2\text{O} \rightarrow 2\text{Fe}(\text{OH})_3 + 4\text{SO}_4^{2-} + 4\text{H}^+$	$R_{\text{FeS}_2\text{O}_x}$
$2\text{Fe}^{2+} + \text{MnO}_2 + 4\text{H}_2\text{O} \rightarrow 2\text{Fe}(\text{OH})_3 + \text{Mn}^{2+} + 2\text{H}^+$	$R_{\text{FeMnO}_2}$
$\text{MnO}_2 + \text{HS}^- + 3\text{H}^+ \rightarrow \text{Mn}^{2+} + \text{S}^0 + 2\text{H}_2\text{O}$	$R_{\text{MnO}_2\text{S}}$
$4\text{MnO}_2 + \text{NH}_4^+ + 6\text{H}^+ \rightarrow 4\text{Mn}^{2+} + \text{NO}_3^- + 5\text{H}_2\text{O}$	$R_{\text{MnNH}_4}$
$5\text{Mn}^{2+} + 2\text{NO}_3^- + 4\text{H}_2\text{O} \rightarrow 5\text{MnO}_2 + \text{N}_2 + 8\text{H}^+$	$R_{\text{MnNO}_3}$
$2\text{Fe}(\text{OH})_3 + \text{H}_2\text{S} + 4\text{CO}_2 \rightarrow 2\text{Fe}^{2+} + \text{S}^0 + 4\text{HCO}_3^- + 2\text{H}_2\text{O}$	$R_{\text{SFe}_3}$
$\text{Fe}_3(\text{PO}_4)_2 + 3\text{H}_2\text{S} \rightarrow 3\text{FeS} + 2\text{H}_3\text{PO}_4$	$R_{\text{Sviv}}$
$\text{FeCO}_3 + \text{H}_2\text{S} \rightarrow \text{FeS} + \text{CO}_2 + \text{H}_2\text{O}$	$R_{\text{SFeCO}_3}$
$\text{FeS} + \text{H}_2\text{S} \rightarrow \text{FeS}_2 + \text{H}_2$	$R_{\text{FeSHS}}$
$\text{FeS} + \text{S}^0 \rightarrow \text{FeS}_2$	$R_{\text{pyr}}/R'_{\text{pyr}}$
$4\text{S}^0 + 4\text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 3\text{HS}^- + 5\text{H}^+$	$R_{\text{S}^0\text{disp}}$
<i>Mineral precipitation reactions</i>	
$\text{Fe}^{2+} + \text{HCO}_3^- + \text{HS}^- \leftrightarrow \text{FeS} + \text{CO}_2 + \text{H}_2\text{O}$	$R_{\text{FeS}}/R'_{\text{FeS}}$
$3\text{Fe}^{2+} + 2\text{H}_3\text{PO}_4 \leftrightarrow \text{Fe}_3(\text{PO}_4)_2 + 6\text{H}^+$	$R_{\text{viv}}/R'_{\text{viv}}$
$a\text{Fe}^{2+} + (1-a)\text{Ca}^{2+} + 2\text{HCO}_3^- \leftrightarrow \text{Fe}_a\text{Ca}_{(1-a)}\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$ ( $a=1$ )	$R_{\text{FeCO}_3}/R'_{\text{FeCO}_3}$
$b\text{Mn}^{2+} + (1-b)\text{Ca}^{2+} + 2\text{HCO}_3^- \leftrightarrow \text{Mn}_b\text{Ca}_{(1-b)}\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$ ( $b=0.95$ )	$R_{\text{MnCO}_3}/R'_{\text{MnCO}_3}$
Local equilibrium reactions	
<i>Adsorption</i>	
$\text{H}_3\text{PO}_4 \leftrightarrow \text{H}_3\text{PO}_4(\text{ads})$	$K_{\text{adsP}}$ (see text)
$\text{S-H}^0 + \text{Fe}^{2+} + \text{HCO}_3^- \leftrightarrow \text{S-Fe}^+ + \text{CO}_2 + \text{H}_2\text{O}$	$K_{\text{adsMn}}$ (see text)
$\text{S-H}^0 + \text{Mn}^{2+} + \text{HCO}_3^- \leftrightarrow \text{S-Mn}^+ + \text{CO}_2 + \text{H}_2\text{O}$	$K_{\text{adsFe}}$ (see text)
$\text{NH}_4^+ \leftrightarrow \text{NH}_4^+(\text{ads})$	$K_{\text{adsNH}_4}$ (see text)
$\text{NH}_3 \leftrightarrow \text{NH}_3(\text{ads})$	$K_{\text{adsNH}_3}$ (see text)
<i>Acid-base reactions</i>	
$\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+$	$K_{\text{C1}} = [\text{H}^+][\text{HCO}_3^-]/[\text{CO}_2]$
$\text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}^+$	$K_{\text{C2}} = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-]$
$\text{NH}_4^+ \leftrightarrow \text{NH}_3 + \text{H}^+$	$K_{\text{NH}} = [\text{H}^+][\text{NH}_3]/[\text{NH}_4^+]$
$\text{H}_2\text{S} \leftrightarrow \text{HS}^- + \text{H}^+$	$K_{\text{HS}} = [\text{H}^+][\text{HS}^-]/[\text{H}_2\text{S}]$
$\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-$	$K_{\text{W}} = [\text{H}^+][\text{OH}^-]$
<i>Equilibrium constants</i>	

Here, the summation accounts for adsorption onto three different substrates: Mn oxides, Fe oxyhydroxides, and a “background” solid, which collectively represents all other solid sediment surfaces. The constants  $K_{\text{Fe},j}^*$  and  $K_{\text{Mn},i}^*$  characterize adsorption of the corresponding ions on the  $i$ th substrate,  $S_{\text{T},i}$  is the total concentration of all sorption sites on the substrate surface minus the number of sites complexed by ions other than protons (mol of sites per gram of substrate), and  $X_i$  is the substrate mass fraction in the sediment. Equations (A1.6 and A1.7) were

obtained from expressions of Van Cappellen and Wang (1996) by including proton concentration in the definition of the apparent stability constants of the surface complexes.

By analogy, the adsorption coefficient for phosphate  $K_{\text{adsP}}$  is defined as

$$[\text{adsP}] = K_{\text{adsP}}[\text{P}_{\text{diss}}] \quad (\text{A1.8})$$

where

Table A1.2. Rate laws for the model reactions.

**Primary redox reactions**For  $i,j = \{O_2, NO_3, MnO_2, Fe(OH)_3, SO_4\}$ ,

$$R_i = (k_{OM1}[OM1] + k_{OM2}[OM2])f_i$$

$$\text{where } f_i = \frac{C_i}{C_i + C_{i,lim}} \prod_{j=1}^{i-1} \frac{C_j^{inh}}{C_j + C_j^{inh}}, f_{CH_4} = 1 - \sum_{j=1}^5 f_j$$

**Secondary redox reactions**

$$R_{FeOx} = k_{FeOx}[Fe^{2+}][O_2]$$

$$R_{surFe} = k_{surFe}[adsFe][O_2]$$

$$R_{NH_4Ox} = k_{NH_4Ox}[TN][O_2], \text{ where } [TN] = [NH_4^+] + [NH_3]$$

$$R_{SOx} = k_{SOx}[TS][O_2], \text{ where } [TS] = [H_2S] + [HS^-]$$

$$R_{FeSOx} = k_{FeSOx}[FeS][O_2]$$

$$R_{FeS_2Ox} = k_{FeS_2Ox}[FeS_2][O_2]$$

$$R_{FeMnO_2} = k_{FeMnO_2}[Fe^{2+}][MnO_2]$$

$$R_{MnO_2S} = k_{MnO_2S}[MnO_2][TS]$$

$$R_{MnNH_4} = k_{MnNH_4}[MnO_2][TN]$$

$$R_{MnNO_3} = k_{MnNO_3}[Mn^{2+}][NO_3^-]$$

$$R_{SFe_3} = k_{SFe_3}[TS][Fe(OH)_3]$$

$$R_{Sviv} = k_{Sviv}[TS][Fe_3(PO_4)_2]$$

$$R_{SFeCO_3} = k_{SFeCO_3}[TS][FeCO_3]$$

$$R_{FeSHS} = k_{FeSHS}[FeS][TS]$$

$$R_{pyr} = k_{pyr}[FeS][S_0]; R'_{pyr} = k'_{pyr}[FeS_2]$$

$$R_{S^0disp} = k_{S^0disp}[S_0]$$

**Mineral precipitation reactions** (Here,  $H(x)=1$  for  $x>0$  and  $H(x)=0$  for  $x\leq 0$ )

$$R_{FeS} = k_{FeS}(\Omega_{FeS} - 1)H(\Omega_{FeS} - 1)$$

$$R'_{FeS} = k'_{FeS}[FeS](1 - \Omega_{FeS})H(1 - \Omega_{FeS})$$

$$\text{where } \Omega_{FeS} = \frac{[Fe^{2+}][HS^-]}{K_{FeS}[H^+]}, \text{ and } [HS^-] = \frac{[TS]}{1 + [H^+]/K_{HS}}$$

$$R_{viv} = k_{viv}(\Omega_{viv}^\alpha - 1)H(\Omega_{viv}^\alpha - 1)$$

$$R'_{viv} = k'_{viv}[Fe_3(PO_4)_2](1 - \Omega_{viv}^\alpha)H(1 - \Omega_{viv}^\alpha),$$

$$\text{where } \Omega_{viv} = \frac{[Fe^{2+}]^3[P_{diss}]^2}{K_{viv}}, \text{ and } \alpha = 1/5$$

$$R_{FeCO_3} = k_{FeCO_3}(\Omega_{FeCO_3} - 1)H(\Omega_{FeCO_3} - 1)$$

$$R'_{FeCO_3} = k'_{FeCO_3}[FeCO_3](1 - \Omega_{FeCO_3})H(1 - \Omega_{FeCO_3})$$

$$\text{where } \Omega_{FeCO_3} = \frac{[Fe^{2+}][CO_3^{2-}]}{aK'_{FeCO_3}}$$

$$\text{and } [CO_3^{2-}] = \frac{[TC]}{1 + [H^+]/K_{C2} + [H^+]^2/K_{C1}K_{C2}}$$

$$R_{MnCO_3} = k_{MnCO_3}(\Omega_{MnCO_3} - 1)H(\Omega_{MnCO_3} - 1)$$

$$R'_{MnCO_3} = k'_{MnCO_3}[MnCO_3](1 - \Omega_{MnCO_3})H(1 - \Omega_{MnCO_3})$$

$$\text{where } \Omega_{MnCO_3} = \frac{[Mn^{2+}][CO_3^{2-}]}{bK'_{MnCO_3}}$$

$$K_{adsP} = \sum_i \frac{K_{P_i}^* X_i S_{Ti}}{[OH^-] + K_{P_i}^* [P_{diss}]} \quad (A1.9)$$

Here,  $[P_{diss}] = [H_3PO_4]$  is the total dissolved (all ionic species combined) phosphate concentration (in mol cm<sup>-3</sup>) and  $[adsP]$  is the concentration of adsorbed phosphate (in mol g<sup>-1</sup> dry wt). A more rigorous derivation that takes into account speciation of both phosphate ions and sorption sites leads to an expression similar to Eq. (A1.9) but with a slightly smaller  $K_{adsP}$  for pH < 7 (Katsev et al. 2006).

Adsorption of reduced nitrogen species is described by the linear partitioning coefficients  $K_{adsNH_4}$  and  $K_{adsNH_3}$ , which relate the concentrations of adsorbed and dissolved

NH<sub>4</sub><sup>+</sup> and NH<sub>3</sub>, respectively (Van Cappellen and Wang 1996).

The depth dependence of the bioturbation coefficient,  $D_b(x)$ , is approximated by

$$D_b(x) = D_b^0 \frac{1 - \tanh((x - H)/\tau_b)}{1 - \tanh(-H/\tau_b)} \quad (A1.10)$$

where  $D_b^0$  is the value at the sediment surface,  $H$  is the depth of the steepest gradient of  $D_b(x)$  within the sediment, and  $\tau_b$  is the characteristic depth half-interval within which most of the decrease in  $D_b(x)$  occurs. For simplicity, we neglected  $D_b$  dependence on the sediment temperature, as well as the differences between the bioturbation rates for solid and liquid species (Fossing et al. 2004).

The bioirrigation coefficient is approximated (Boudreau 1997) by

$$\alpha_{irr}(x) = \alpha_{irr}^0 \exp(-x/\tau_{irr}) \quad (A1.11)$$

where parameters  $\alpha_{irr}^0$  and  $\tau_{irr}$  describe the bioirrigation intensity at the interface and its depth attenuation, respectively.

Because reduced species precipitate at the oxidized burrow walls, they do not penetrate the burrows and therefore experience effectively lower bioirrigation rates than oxidized species. Some previous studies have accounted for this effect by introducing a correction factor for the bioirrigation coefficient  $\alpha_{irr}^0$  (e.g., Berg et al. 2003). It is, however, more appropriate to correct the concentration in the burrow, rather than the bioirrigation coefficient, since the latter effectively characterizes the activity of irrigating organisms and therefore should not be species-dependent. The bioirrigation term in Eq. (A1.1a) reflects this argument. The two approaches produce similar results when the concentration of solute in the overlying water,  $C_b^0$ , is small, which is typically the case for reduced species. We calculated the concentration  $C_{burr_i}$  in Eq. (A1.1a) by multiplying the pore-water concentration  $C_i$  by a factor of 0.1 for Fe(II), Mn(II), NH<sub>4</sub><sup>+</sup>, and H<sub>2</sub>S, as well as for phosphate, which is known to adsorb to the oxidized iron layer along the burrow walls. For other species,  $C_{burr_i} = C_i$  was used.

**Numerical method**

Nonlinear coupled partial differential equations (A1.1) with boundary conditions (A1.2–A1.4) were discretized on an evenly spaced grid so that the species concentrations at each node were described by a system of ordinary differential equations (ODE). The resulting ODEs were solved with a method-of-lines stiff ODE integrator VODE (Brown et al. 1989) to obtain the species concentrations  $C_i(x,t)$ . Steady-state solutions  $C_{i,st}(x)$  were obtained by running the program for diagenesis times sufficiently long for any transient behaviors to vanish: 10,000 yr in our simulations. Total analytical variables ([TC], [TS], [TN], and [ALK], respectively) were used to characterize the aqueous concentrations of pore-water carbonate, sulfide, ammonium, and alkalinity:

Table A1.3. Parameter values used in the model. Interface concentrations (for solutes) and sedimentation fluxes (for solids) not listed in this table are zero. References: (1) Silverberg et al. (1987); (2) A. Mucci (2003, unpubl. data); (3) Smith and Schafer (1999); (4) Hecky et al. (1993); (5) Silverberg and Sundby (1990); (6) Boudreau (1997); (7) Lucotte and d'Anglejan (1988); (8) Gilbert et al. (2005); (9) Belzile (1987); (10) Edenborn et al. (1987); (11) Sundby et al. (1992); (12) Berg et al. (2003); (13) Van Cappellen and Wang (1996); (14) Pallud and Van Cappellen (2006); (15) Van Cappellen and Wang (1995); (16) Hunter et al. (1998); (17) Stumm and Morgan (1996); (18) Hulth et al. (1999); (19) Wijsman et al. (2002); (20) Meysman et al. (2003); (21) Fossing et al. (2004); (22) Rickard (1997); (23) Morse et al. (1987); (24) Davison (1993); (25) Dzombak and Morel (1990); (26) Boudreau et al. (1998).

Parameter	Value	Units	Typical values	Ref.
Integration depth, $L$	20	cm		
Solid density, $\rho$	2.65	$\text{g cm}^{-3}$		
Sedimentation velocity at interface/deep sediment, $U_0/U_L$	0.54/0.28	$\text{cm yr}^{-1}$	0.5–0.6	1,3
N:C ratio in OM, $y$	0.05	–		11
P:C ratio in OM1/OM2, $z_1/z_2$	0.015/0.004	–	0.002–0.016	4,11
Bioturbation coeff. at surface, $D_b^0$	0.9	$\text{cm}^2 \text{yr}^{-1}$	3–5	1,5
Location of max. bioturbation gradient, $H$	0	cm		
Bioturbation half-interval, $\tau_b$	10	cm		
Bioirrigation coeff. at surface, $\alpha_{\text{irr}}^0$	240	$\text{yr}^{-1}$	10–200	6
Bioirrigation half-depth, $\tau_{\text{irr}}$	4	cm		
pH at interface (calculated)	7.5		7.2–7.5	7
Sediment temperature, $T$	5	$^{\circ}\text{C}$		
Water depth	300	m	250–300	
$[\text{O}_2]^0$	$8 \times 10^{-7}$	$\text{mol cm}^{-3}$	(0.6– 0.8) $\times 10^{-7}$	1,8
$[\text{NO}_3]^0$	$2.5 \times 10^{-8}$	$\text{mol cm}^{-3}$	$(0.5\text{--}3) \times 10^{-8}$	2,8,9
$[\text{SO}_4]^0$	$2.8 \times 10^{-5}$	$\text{mol cm}^{-3}$	$2.8 \times 10^{-5}$	10
$[\text{TC}]^0$	$2.44 \times 10^{-6}$	$\text{mol cm}^{-3}$		
$[\text{ALK}]^0$	$2.40 \times 10^{-6}$	$\text{mol cm}^{-3}$		
$[\text{H}_3\text{PO}_4]^0$	$2 \times 10^{-9}$	$\text{mol cm}^{-3}$	$2 \times 10^{-9}$	11
Flux of reactive OM, $F_{OM1}$	$1 \times 10^{-4}$	$\text{mol cm}^2 \text{yr}^{-1}$	$<(3.7\text{--}$ $5.8) \times 10^{-4}$	1
Flux of refractory OM, $F_{OM2}$	$2.3 \times 10^{-4}$	$\text{mol cm}^2 \text{yr}^{-1}$	$<(3.7\text{--}$ $5.8) \times 10^{-4}$	1
Total ( $\Phi_{\text{sed,Fe}}$ ) flux of reactive Fe(III) at reference steady state, $F_{\text{Fe}(\text{OH})_3}$	$2 \times 10^{-5}$	$\text{mol cm}^{-2} \text{yr}^{-1}$		
Total ( $\Phi_{\text{sed,Mn}}$ ) flux of reactive Mn oxide at reference steady state, $F_{\text{MnO}_2}$	$1.4 \times 10^{-5}$	$\text{mol cm}^{-2} \text{yr}^{-1}$	$<1.4 \times 10^{-5}$	5
Reactivity of OM1, $k_{OM1}$	1.8	$\text{yr}^{-1}$	0.1–80	12,6
Reactivity of OM2, $k_{OM2}$	0.02	$\text{yr}^{-1}$	$(5\text{--}500) \times 10^{-5}$	6
Monod constant, $C_{\text{O}_2}^{\text{lim}}$	$1.0 \times 10^{-9}$	$\text{mol cm}^{-3}$	$10^{-10}\text{--}10^{-8}$	13
Monod constant, $C_{\text{NO}_3}^{\text{lim}}$	$5.0 \times 10^{-8}$	$\text{mol cm}^{-3}$	$(2\text{--}80) \times 10^{-9}$	12
Monod constant, $C_{\text{MnO}_2}^{\text{lim}}$	$1.0 \times 10^{-6}$	$\text{mol g}^{-1}$	$(4\text{--}32) \times 10^{-6}$	12
Monod constant, $C_{\text{Fe}(\text{OH})_3}^{\text{lim}}$	$8.0 \times 10^{-5}$	$\text{mol g}^{-1}$	$10^{-10}\text{--}10^{-4}$	13
Monod constant, $C_{\text{SO}_4}^{\text{lim}}$	$1.0 \times 10^{-5}$	$\text{mol cm}^{-3}$	$10^{-7}\text{--}10^{-6}$	13,14
<i>Reaction rate constants</i>				
$k_{\text{FeOx}}$	$0.35 \times 10^{11}$	$\text{cm}^3 \text{mol}^{-1} \text{yr}^{-1}$		13
$k_{\text{surFe}}$	$1.25 \times 10^{10}$	$\text{cm}^3 \text{mol}^{-1} \text{yr}^{-1}$		
$k_{\text{NH}_4\text{Ox}}$	$5 \times 10^9$	$\text{cm}^3 \text{mol}^{-1} \text{yr}^{-1}$	$5 \times 10^9$	13
$k_{\text{SO}_x}$	$1.6 \times 10^{10}$	$\text{cm}^3 \text{mol}^{-1} \text{yr}^{-1}$	$>1.6 \times 10^8$	13
$k_{\text{FeSO}_x}$	$1.0 \times 10^9$	$\text{cm}^3 \text{mol}^{-1} \text{yr}^{-1}$	$10^8\text{--}10^{10}$	15,16
$k_{\text{FeS}_2\text{Ox}}$	$2 \times 10^8$	$\text{cm}^3 \text{mol}^{-1} \text{yr}^{-1}$	$10^8$	19,21
$k_{\text{FeMnO}_2}$	$3.0 \times 10^9$	$\text{cm}^3 \text{mol}^{-1} \text{yr}^{-1}$	$10^6\text{--}3 \times 10^9$	12,13,17
$k_{\text{MnO}_2\text{S}}$	$2.0 \times 10^7$	$\text{cm}^3 \text{mol}^{-1} \text{yr}^{-1}$	$(1\text{--}2) \times 10^7$	13,16
$k_{\text{MnNH}_4}$	$1.0 \times 10^6$	$\text{cm}^3 \text{mol}^{-1} \text{yr}^{-1}$	$10^5\text{--}10^6$	18
$k_{\text{MnNO}_3}$	$1.0 \times 10^{10}$	$\text{cm}^3 \text{mol}^{-1} \text{yr}^{-1}$	$10^5\text{--}10^6$	26
$k_{\text{SFe}_3}$	$4 \times 10^7$	$\text{cm}^3 \text{mol}^{-1} \text{yr}^{-1}$	$10^2\text{--}10^8$	16,19,20
$k_{\text{Sviv}}$	$7.0 \times 10^7$	$\text{cm}^3 \text{mol}^{-1} \text{yr}^{-1}$		
$k_{\text{SFeCO}_3}$	$5.0 \times 10^7$	$\text{cm}^3 \text{mol}^{-1} \text{yr}^{-1}$		
$k_{\text{FeSHS}}$	$8.0 \times 10^6$	$\text{cm}^3 \text{mol}^{-1} \text{yr}^{-1}$	$10^6\text{--}10^{10}$	21,22
$k_{\text{pyr}}$	$1.0 \times 10^5$	$\text{g mol}^{-1} \text{yr}^{-1}$		21
$k'_{\text{pyr}}$	0.01	$\text{yr}^{-1}$		13
$k_{\text{S}^0\text{disp}}$	0.12	$\text{yr}^{-1}$	0.1–22	12,21
$k_{\text{FeS}}$	$0.3 \times 10^{-5}$	$\text{mol g}^{-1} \text{yr}^{-1}$	$10^{-7}\text{--}10^{-4}$	13,16
$k'_{\text{FeS}}$	$1.0 \times 10^{-3}$	$\text{yr}^{-1}$		13

Table A1.3. Continued.

Parameter	Value	Units	Typical values	Ref.
$K_{\text{FeS}}$	$2.51 \times 10^{-6}$	$\text{mol cm}^{-3}$		23
$k_{\text{FeCO}_3}$	$0.8 \times 10^{-6}$	$\text{mol g}^{-1} \text{yr}^{-1}$		13
$k'_{\text{FeCO}_3}$	0.25	$\text{yr}^{-1}$		13
$k''_{\text{FeCO}_3}$	$4.0 \times 10^{-15}$	$(\text{mol cm}^{-3})^2$		
$k_{\text{MnCO}_3}$	$0.1 \times 10^{-5}$	$\text{mol g}^{-1} \text{yr}^{-1}$	$(1-100) \times 10^{-4}$	13
$k'_{\text{MnCO}_3}$	0.25	$\text{yr}^{-1}$	$10^{-2}-10^3$	13
$K_{\text{MnCO}_3}$	$2.162 \times 10^{-14}$	$(\text{mol cm}^{-3})^2$		
$k_{\text{viv}}$	$0.7 \times 10^{-9}$	$\text{mol g}^{-1} \text{yr}^{-1}$		
$k'_{\text{viv}}$	1.0	$\text{yr}^{-1}$		
$K_{\text{viv}}$	$3.0 \times 10^{-50}$	$(\text{mol cm}^{-3})^5$		24
<i>Equilibrium adsorption constants</i>				
$K_{\text{FeonFe}}^*$	$1 \times 10^{-3}$	–	$< 2 \times 10^{-3}$	25
$K_{\text{FeonMn}}^*$	$1 \times 10^{-5}$	–	$< 2 \times 10^{-3}$	25
$K_{\text{FeonB}}^*$	$1.0 \times 10^{-5}$	–		
$K_{\text{MnonFe}}^*$	$3 \times 10^{-6}$	–		
$K_{\text{MnonMn}}^*$	$3 \times 10^{-5}$	–		
$K_{\text{MnonB}}^*$	$1.0 \times 10^{-5}$	–		
$K_{\text{PonFe}}^*$	$3.0 \times 10^{-3}$	–	$< 2 \times 10^{-3}$	25
$K_{\text{PonB}}^*$	$2.0 \times 10^{-6}$	–		
$K_{\text{adsNH}_4}, K_{\text{adsNH}_3}$	1.4	–		13
$S_{\text{TFe}}, S_{\text{TMn}}$	$1.0 \times 10^{-2}$	$\text{mol g}^{-1}$		
$S_{\text{TB}}$	$3.0 \times 10^{-5}$	$\text{mol g}^{-1}$		

Table A1.4. Local sensitivity analysis for steady-state fluxes at reference state. Variations (in %) are given for the steady-state fluxes of dissolved iron, manganese, nitrate, oxygen, and total phosphate in response to a 10% increase in the values of individual model parameters relative to their respective values at reference steady state (Table A1.3).

Parameter	$\text{H}_3\text{PO}_4$	$\text{Fe}^{2+}$	$\text{Mn}^{2+}$	$\text{NO}_3^-$	$\text{O}_2$
$F_{\text{OM1}}$	7.227	2.204	6.985	4.805	4.428
$F_{\text{OM2}}$	5.813	3.737	4.486	1.317	0.835
$U$	-3.203	-12.511	-3.664	-1.149	-1.185
$D_b^0$	0.058	-1.161	0.332	0.200	-0.809
$\alpha_{\text{irr}}^0$	-1.139	-1.196	-3.518	4.212	2.931
$\tau_{\text{irr}}$	-2.855	3.928	1.110	7.507	3.541
$[\text{O}_2]^0$	-1.814	-11.745	-11.801	-6.841	4.842
$[\text{NO}_3^-]^0$	-0.500	-5.137	-4.862	9.619	-0.443
$F_{\text{Fe}(\text{OH})_3}$	-5.301	21.170	-1.313	-0.118	0.004
$F_{\text{MnO}_2}$	-0.342	-0.954	7.093	0.274	0.103
$k_{\text{OM1}}$	-0.572	-1.041	-2.254	-0.450	1.198
$k_{\text{OM2}}$	2.881	3.615	2.950	1.195	0.705
$C_{\text{O}_2}^{\text{lim}}$	0.031	-0.343	-0.382	0.151	-0.062
$C_{\text{Fe}^{\text{II}}}^{\text{lim}}$	0.015	-7.974	-0.626	-0.024	-0.011
$C_{\text{MnO}_2}^{\text{lim}}$	-0.004	-0.604	-0.398	-0.036	-0.012
$k_{\text{MnFe}}$	-0.008	-0.622	-0.257	-0.008	-0.004
$C_{\text{NO}_3}^{\text{lim}}$	0.033	-0.245	-0.319	-0.278	0.030
$k_{\text{FeS}}$	0.043	-1.339	-0.288	-0.012	-0.005
$K_{\text{FeonFe}}^*$	-0.008	-0.675	-0.363	-0.017	-0.004
$K_{\text{FeonMn}}^*$	0.020	-0.012	-0.266	-0.011	-0.004
$K_{\text{FeonB}}^*$	0.012	-0.276	-0.321	-0.014	-0.005
$K_{\text{MnonFe}}^*$	-0.004	0.014	0.035	-0.052	0.010
$K_{\text{MnonMn}}^*$	0.004	-0.053	-0.263	-0.210	0.038
$K_{\text{MnonB}}^*$	-0.002	-0.023	0.136	-0.026	0.010
$K_{\text{PonFe}}^*$	-0.095	-0.160	-0.287	-0.012	-0.004
$K_{\text{PonB}}^*$	0.016	-0.011	-0.266	-0.011	-0.004
$C_{\text{SO}_4}^{\text{lim}}$	-1.122	3.324	0.074	-0.009	-0.005
$K_{\text{FeSHS}}$	-0.568	0.472	-0.320	-0.013	-0.005

Table A1.5. Parameter ranges used in the sensitivity analysis of transient solutions.

	Notation	Value in ref. state	Units	Min. value	Max. value
Recycling coeff. for Fe	$\varepsilon_{\text{Fe}}$	–	–	0	1
Recycling coeff. for Mn	$\varepsilon_{\text{Mn}}$	–	–	0	1
Reactive organic matter (OM) flux	$F_{\text{OM1}}$	$1.02 \times 10^{-4}$	$\text{mol cm}^{-2} \text{ yr}^{-1}$	$0.82 \times 10^{-4}$	$1.22 \times 10^{-4}$
Refractory OM flux	$F_{\text{OM2}}$	$2.33 \times 10^{-4}$	$\text{mol cm}^{-2} \text{ yr}^{-1}$	$1.87 \times 10^{-4}$	$2.80 \times 10^{-4}$
Flux of reactive Fe(III)	$F_{\text{Fe(OH)}_3}$	$2.04 \times 10^{-5}$	$\text{mol cm}^{-2} \text{ yr}^{-1}$	$1.63 \times 10^{-5}$	$2.45 \times 10^{-5}$
Flux of $\text{MnO}_2$	$F_{\text{MnO}_2}$	$1.46 \times 10^{-5}$	$\text{mol cm}^{-2} \text{ yr}^{-1}$	$1.17 \times 10^{-5}$	$1.75 \times 10^{-5}$
Burial velocity (at depth)	$U_L$	0.28	$\text{cm yr}^{-1}$	0.224	0.336
Bioturbation coeff. (at sediment–water interface)	$D_b^0$	0.9	$\text{cm}^2 \text{ yr}^{-1}$	0.72	1.08
Bioirrigation coeff. (at sediment–water interface)	$\alpha_{\text{irr}}^0$	240	$\text{yr}^{-1}$	192	289
Bioirrigation half-depth	$\tau_{\text{irr}}$	4	cm	3.2	4.8
Coefficient in Eq. (2)	$K_{\text{DbO}_2}$	–	$\mu\text{mol L}^{-1}$	0	100

$$[\text{TC}] = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (\text{A1.12})$$

$$[\text{TS}] = [\text{HS}^-] + [\text{H}_2\text{S}] \quad (\text{A1.13})$$

$$[\text{TN}] = [\text{NH}_4^+] + [\text{NH}_3] \quad (\text{A1.14})$$

$$\begin{aligned} [\text{ALK}] = & [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{HS}^-] \\ & - [\text{NH}_4^+] + F[\text{adsFe}] + F[\text{adsMn}] \\ & - [\text{H}^+] + [\text{OH}^-] \end{aligned} \quad (\text{A1.15})$$

The equilibrium constants for the relevant acid–base reactions (Table A1.1) were calculated using expressions in Boudreau (1997) and Millero (1995), corrected for temperature, salinity, and pressure.

We assumed that the adsorption reactions are in local chemical equilibrium so that the amounts of Fe(II), Mn(II), and phosphate can be expressed as total (dissolved + adsorbed) quantities:

$$\begin{aligned} [\text{tFe}] = & [\text{Fe}^{2+}] + [\text{adsFe}]F \\ = & [\text{Fe}^{2+}](1 + FK_{\text{adsFe}}) \end{aligned} \quad (\text{A1.16})$$

$$\begin{aligned} [\text{tMn}] = & [\text{Mn}^{2+}] + [\text{adsMn}]F \\ = & [\text{Mn}^{2+}](1 + FK_{\text{adsMn}}) \end{aligned} \quad (\text{A1.17})$$

$$\begin{aligned} [\text{tP}] = & [\text{P}_{\text{diss}}] + [\text{adsP}]F \\ = & [\text{P}_{\text{diss}}](1 + FK_{\text{adsP}}) \end{aligned} \quad (\text{A1.18})$$

The conversion factor  $F$  between the concentration units for solid and liquid species is  $F = \rho(1 - \varphi)/\varphi$ . The terms  $F[\text{adsFe}]$  and  $F[\text{adsMn}]$  in the expression for total alkalinity [ALK] (Eq. A1.15) accounts for the release of  $\text{H}^+$  in the  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  sorption/desorption reactions, respectively (Table A1.1).

The model solves the diagenetic equation Eq. A1.1 for the following species: OM1, OM2,  $\text{MnO}_2$ ,  $\text{Fe(OH)}_3$ , FeS,

$\text{FeS}_2$ ,  $\text{S}^0$ ,  $\text{Fe}_a\text{Ca}_{(1-a)}\text{CO}_3$ ,  $\text{Mn}_b\text{Ca}_{(1-b)}\text{CO}_3$ , vivianite,  $\text{O}_2$ , TC, TS, TN, ALK,  $\text{SO}_4^{2-}$ ,  $\text{CH}_4$ , tFe, tMn, and tP. The reaction set in Table A1.1 is closed in terms of the species mass balance, with the exception of  $\text{H}_2$  generated in the reaction of pyrite formation. Hydrogen can be oxidized in the sediment by a suite of pathways (Meysman et al. 2003). However, in the absence of kinetic information, and because, at our study site, these reactions can constitute only a small fraction of total consumption of electron acceptors, we neglected hydrogen oxidation.

Since the adsorption coefficients (Eqs. A1.6–A1.9) depend on the proton concentration  $[\text{H}^+]$ , which, in turn, cannot be determined independently of  $[\text{adsFe}]$  and  $[\text{adsMn}]$  (because  $[\text{adsFe}]$ ,  $[\text{adsMn}]$ , and  $[\text{H}^+]$  enter Eq. A1.15), a Newton–Raphson algorithm was employed to determine the concentrations  $[\text{Fe}^{2+}]$ ,  $[\text{Mn}^{2+}]$ , and  $[\text{H}^+]$  at each iteration step by simultaneously solving Eqs. A1.15–A1.17 with known [ALK], [tFe] and [tMn], together with Eqs. A1.6–A1.9 and the equilibrium relations in Table A1.1. Concentrations of all other equilibrium species were calculated from the equilibrium speciation relations in Table A1.1 and the sorption relations (A1.6–A1.9).

## Sensitivity analyses

Table A1.4 presents the results of a local sensitivity analysis of model solutions at steady state (as described in the main article text). Table A1.5 specifies the parameter ranges that were used in the sensitivity analysis of transient solutions.

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