Electronic Supplementary Material

Advancing on large-scale trends of apparent organic matter reactivity in marine sediments and patterns of benthic carbon transformation

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Table S1. Reaction network governing heterotrophic organic matter degradation in marine sediments implemented in the Reaction-Transport Model (Adapted from Aguilera et al., 2005; Thullner et al., 2009; Wehrmann et al., 2013).

	Reaction Pathway	Stoichiometry	Reaction rate
		Primary redox reactions	
r_1	Aerobic OM degradation	$(CH_2O)_x(NH_3)_y(H_3PO_4)_z + (x+2y)O_2 + (y+2z)HCO_3^- \rightarrow (x+y+2z)CO_2 + yNH_4^+ + zHPO_4^{2-} + (x+y+2z)H_2O$	$r_1 = v \cdot (a+age)^{-1} \cdot CH_2O \cdot f_{O_2}$
r_2	Denitrification	$(CH_2O)_x(NH_3)_y(H_3PO_4)_z + \left(\frac{4x+3y}{5}\right)NO_3^- \rightarrow \left(\frac{2x+4y}{5}\right)N_2 + \left(\frac{x-3y+10z}{5}\right)CO_2 + \left(\frac{4x+3y-10z}{5}\right)HCO_3^- + zPO_4^{2-} + \left(\frac{3x+6y+10z}{5}\right)H_2O$	$r_2 = v \cdot (a+age)^{-1} \cdot CH_2O \cdot f_{NO_3}$
r_3	Sulfate reduction	$(CH_2O)_x(NH_3)_y(H_3PO_4)_z + \frac{x}{2}SO_4^{2-} + (y-2z)CO_2 + (y-2z)H_2O \rightarrow (x+y-2z)HCO_3^- + yNH_4^+ + zHPO_4^{2-} + \frac{x}{2}H_2S$	$r_3 = v \cdot (a+age)^{-1} \cdot CH_2O \cdot f_{SO_4^{2-}}$
r_4	Methanogenesis	$(CH_2O)_x(NH_3)_y(H_3PO_4)_z + (y-2z)H_2O \rightarrow \left(\frac{x-2y+4z}{2}\right)CO_2 + (y-2z)HCO_3^- + yNH_4^+ + zHPO_4^{2-} + \frac{x}{2}CH_4$	$r_4 = v \cdot (a+age)^{-1} \cdot CH_2O \cdot f_{CH_4}$
		Secondary redox reactions	
r_5	Ammonium oxidation by oxygen	$NH_4^+ + 2O_2 + 2HCO_3^- \rightarrow NO_3^- + 3H_2O$	$r_5 = k_5 \cdot NH_4^+ \cdot O_2$
r_6	Sulfide oxidation by oxygen	$H_2S + 2O_2 + 2HCO_3^- \rightarrow SO_4^{2-} + 2CO_2 + 2H_2O$	$r_6 = k_6 \cdot (HS^- + H_2S) \cdot O_2$
r_7	Anaerobic oxidation of methane (AOM)	$CH_4 + CO_2 + SO_4^{2-} \rightarrow 2HCO_3^- + H_2S$	$r_7 = k_7 \cdot CH_4 \cdot SO_4^{2-}$
r_8	Methane oxidation by oxygen	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	$r_8 = k_8 \cdot CH_4 \cdot O_2$

Table S2. Kinetic rate laws controlling the reaction network (Adapted from Jourabchi, 2005).

	Kinetic rate laws
r_1	$\begin{cases} f_{O_2} = 1 \text{ for } O_2 > K_{O_2} \\ f_{O_2} = \dfrac{O_2}{K_{O_2}} \text{ for } O_2 \leq K_{O_2} \end{cases}$
r_2	$\begin{cases} f_{NO_3^-} = 0 \text{ for } f_{O_2} = 1 \\ f_{NO_3^-} = \left(1 - f_{O_2}\right) \text{ for } f_{O_2} < 1 \text{ and } NO_3^- > K_{NO_3^-} \\ f_{NO_3^-} = \left(1 - f_{O_2}\right)\dfrac{NO_3^-}{K_{NO_3^-}} \text{ for } f_{O_2} < 1 \text{ and } NO_3^- \leq K_{NO_3^-} \end{cases}$
r_3	$\begin{cases} f_{SO_4^{2-}} = 0 \text{ for } f_5 \equiv f_{O_2} + f_{NO_3^-} = 1 \\ f_{SO_4^{2-}} = (1 - f_5) \text{ for } f_5 < 1 \text{ and } SO_4^{2-} > K_{SO_4^{2-}} \\ f_{SO_4^{2-}} = (1 - f_5)\dfrac{SO_4^{2-}}{K_{SO_4^{2-}}} \text{ for } f_5 < 1 \text{ and } SO_4^{2-} \leq K_{SO_4^{2-}} \end{cases}$
r_4	$f_{CH_4} = \left(1 - \left(f_{O_2} + f_{NO_3^-} + f_{SO_4^{2-}}\right)\right)$

Table S3. Model parameters and boundary conditions adopted in the sensitivity analyses used to determine the minimum dataset necessary to constrain apparent organic matter reactivity k based on the Reactive Continuum Model parameters a and v.

Parameter	***Symbol***	***Unit***	***Value***
Transport Parameters			
Model domain	L	cm	150
Bioirrigation coefficient	α_0	y^{-1}	10
Bioirrigation attenuation depth	x_{irr}	cm	3.5
Bioturbation depth	z_{bio}	cm	10
Bioturbation coefficient	D_{bio}	$cm^2\ y^{-1}$	23.98
Porosity	φ	–	0.47
Sedimentation rate	ω	$cm\ y^{-1}$	0.06
Temperature	T	°C	0.65
Salinity	S	–	35
Water depth	h	m	250
Reaction Parameters			
Stoichiometric coefficients	$x/y/z$	–	106/16/1
Reactive continuum model scaling parameter	a	y	[10^{-2} – 10^{4}]
Reactive continuum model shaping parameter	v	–	[10^{-1} – $\mathrm{l}0^{0}$]
Boundary Conditions			
Particulate organic carbon	POC	wt%	0.32
Oxygen	O_2	µM	325
Nitrate	NO_3^-	µM	9
Sulfate	SO_4^{2-}	mM	28
Ammonium	NH_4^+	µM	0
Sulfides	HS^-	µM	0
Methane	CH_4	µM	0

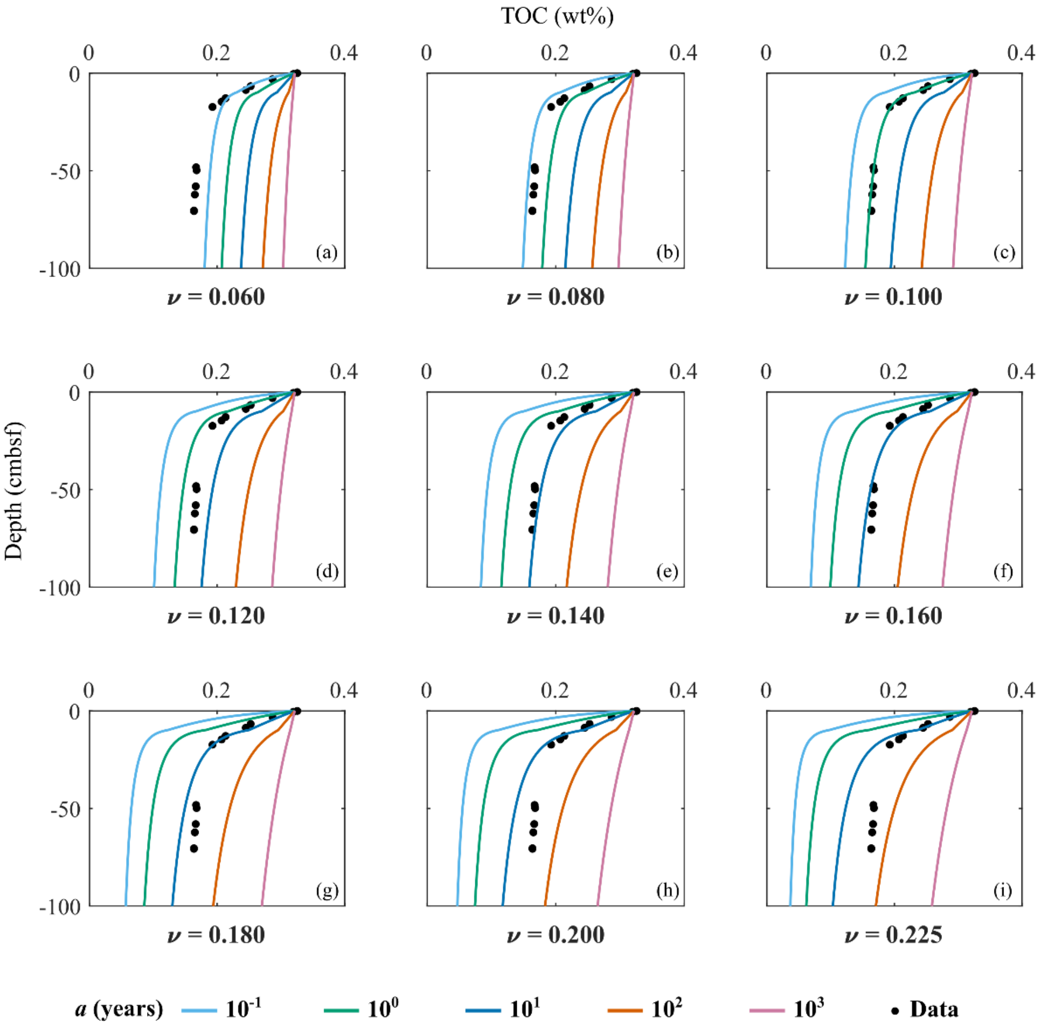

Figure S1. Total organic carbon depth profiles yielded by the sensitivity analysis for an ensemble of scaling parameter ν and shaping parameter a (see Table S3). Based on TOC alone multiple pairs of a and ν would be extracted from the same depth-profile.

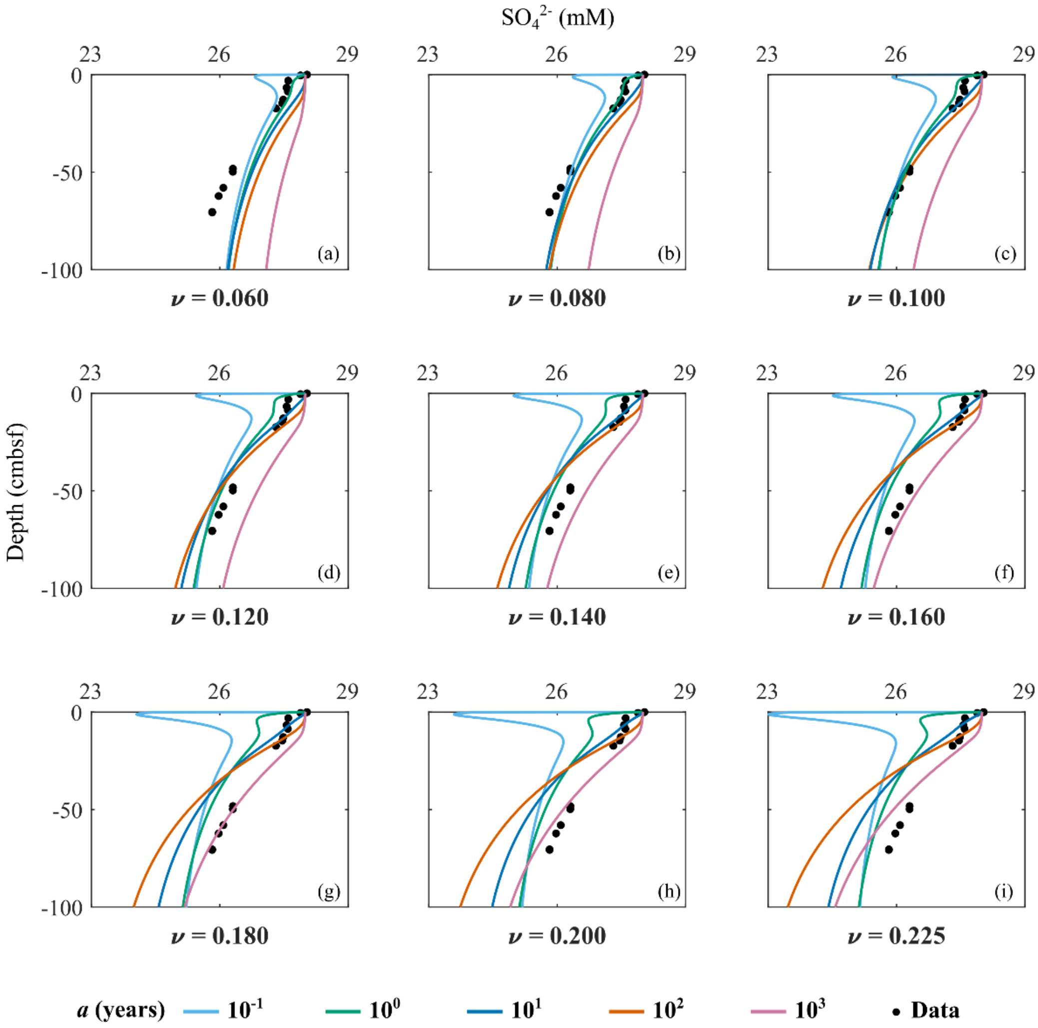

Figure S2. Sulfate depth profiles yielded by the sensitivity analysis for an ensemble of scaling parameter ν and shaping parameter a (see Table S3). Considering SO_4^{2-} alongside TOC improves the determination of a and ν by excluding those pairs that only fit TOC.

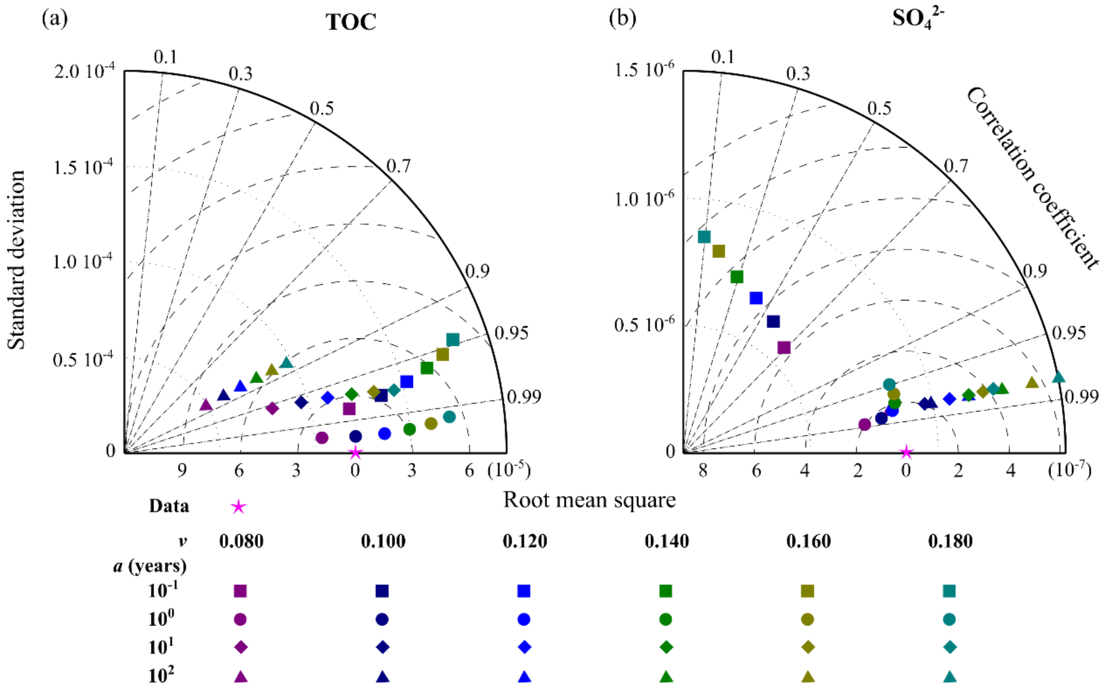

Figure S3. Sensitivity analysis best-fit based on Reactive Continuum model parameters a and v for (a) total organic carbon and (b) sulfate. The adoption of two species (i.e. TOC and SO_4^{2-}) relieves the uncertainties in constraining organic matter reactivity parameters.

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