Comparison of organic matter oxidation approaches in sediment diagenesis models

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Abstract: Sediment diagenesis models have been developed over the past few decades using various algorithms and notation for similar processes. Organic matter oxidation in particular has been parameterised in a number of different ways. The reactions involved are the sequence of decreasing energy-yield oxidation pathways (aerobic mineralisation, denitrification, Mn(IV) reduction, Fe(III) reduction, SO_4^{2-} reduction and methanogenesis). In this paper we examine the differences between three common approaches that have emerged in the literature and quantify whether the differences have a significant effect on organic matter oxidation rates.

Firstly, the equations of three approaches were expressed using a common notation, highlighting the similarities and differences between the rate expressions. All approaches have an oxidation rate that is the product of the rate constant k_{OM}, organic matter concentration OM, a limitation term Θ_{Ox}, and an inhibition term Θ_{In}. The Θ_{Ox} and Θ_{In} of Approach 1 apply Monod kinetics. The Θ_{Ox} and Θ_{In} of Approach 2 apply Blackman kinetics, which has previously been described as not significantly different to a Monod formulation. Approach 3 uses Monod terms while mixing the limitation and inhibition functions differently to Approach 1. While Approaches 1 and 2 usually use six oxidation pathways, Approach 3 uses three pathways, combining manganese, iron and sulfate reduction and methanogenesis into one anoxic pathway. Methanogenesis in Approach 1 is a product of the previous five inhibition terms, whereas in Approach 2 it is the difference between the total rate and the sum of the five higher-energy rates.

The algorithms of the three approaches were compared with a simple calculation of organic matter oxidation on a homogenous unit of sediment over 3 years, in marine and freshwater conditions. The differences between the approaches were illustrated in terms of the points in time when the oxidants are exhausted. In all three approaches, O_2 was exhausted within 1.7 to 1.8 days. The NO_3^- was exhausted after 1.7 to 1.8 days in Approaches 2 and 3, but after 2.8 days in Approach 1. In Approach 1 Mn(IV) was exhausted at day 798 and Fe(III) at day 857, whereas these components were not exhausted in Approach 2 in the three year simulation, and not simulated in Approach 3. In the freshwater experiment, SO_4^{2-} was depleted by days 425 and 215, respectively. While the time to depletion differed considerably, it is of note that both approaches allowed depletion of SO_4^{2-} prior to the more thermodynamically favourable oxidants.

Approaches 1 and 3 allow for more overlap of the rates of different oxidation pathways whereas Approach 2 only allows for overlap when the oxidant concentration is below its limiting concentration. This represents a different conceptualisation of the microbial processes in the sediment with bacteria either partially or completely inhibited. Implications of this include that at the time when the corresponding reduction pathway began in Approach 2, in Approach 1 25% of NO_3^-, 17% of Fe(III) and 1% (marine experiment) or 38% (freshwater experiment) of SO_4^{2-} had already been consumed.

Approaches 1 and 2 exhibited a steady decline in total organic matter oxidation rate as organic matter concentration decreases, whereas in Approach 3 there was an increase in the total rate when denitrification and anoxic processes overlapped due to the lack of inhibition of anoxic processes.
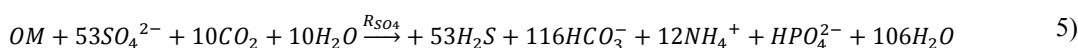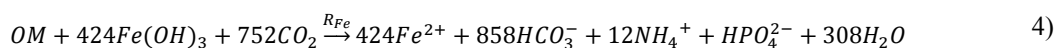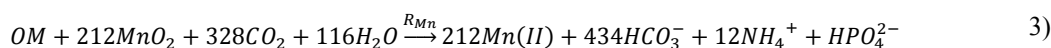
The differences between the approaches are significant enough to suggest that care must be taken in choosing which best represents the modeller's conceptualisation of microbial processes. The effects of secondary reactions and transport processes between sediment layers on the chemical profiles will be tested in future work using a full diagenesis model.

Keywords: *Sediment, diagenesis, reactive transport model, organic matter*

1. INTRODUCTION

Biogeochemical reactions in aquatic sediment can affect the amount of dissolved O_2 in the overlying water and the adsorption or release of contaminants and nutrients. Examples of processes that may be involved include burial of nutrients in the sediment or cycling back to the water column, denitrification, depletion of dissolved O_2 available to aquatic organisms, dissolution and reduction of solid Mn(IV) and Fe(III) and the subsequent release of any nutrients or contaminants adsorbed to their surfaces, generation of H_2S gas or metal sulphides, and generation of CH_4 gas. Numerical models of sediment physical-biogeochemical processes (collectively termed 'early diagenesis') have been developed and applied to unravel the effects of the many competing and interdependent reactions (Boudreau, 1997).

While the models that have been developed over the past few decades started with a common origin (Berner, 1964; Berner, 1980), they have since diverged into several model 'families' that have a similar underlying basis but different algorithms, variables, notation, and parameter values. However, there is limited analysis comparing the differences between the approaches. The focus of this analysis is how three common modelling approaches treat the oxidation of organic matter (OM), as this process governs sediment function and quality. These models all describe OM degradation by a sequence of bacterially-driven reactions with decreasing free energy yield, as described by Froelich *et al.* (1979). The reactions used are taken from Van Cappellen and Wang (1996):

$$OM + 130O_2 + 14HCO_3^- \xrightarrow{R_{O2}} 118CO_2 + 12NO_3^- + HPO_4^{2-} + 132H_2O \qquad 1)$$

$$OM + 92NO_3^- \xrightarrow{R_{NO3}} 52N_2 + 16CO_2 + +90HCO_3^- + HPO_4^{2-} + 80H_2O \qquad 2)$$

$$OM + 212MnO_2 + 328CO_2 + 116H_2O \xrightarrow{R_{Mn}} 212Mn(II) + 434HCO_3^- + 12NH_4^+ + HPO_4^{2-} \qquad 3)$$

$$OM + 424Fe(OH)_3 + 752CO_2 \xrightarrow{R_{Fe}} 424Fe^{2+} + 858HCO_3^- + 12NH_4^+ + HPO_4^{2-} + 308H_2O \qquad 4)$$

$$OM + 53SO_4^{2-} + 10CO_2 + 10H_2O \xrightarrow{R_{SO4}} + 53H_2S + 116HCO_3^- + 12NH_4^+ + HPO_4^{2-} + 106H_2O \qquad 5)$$

$$OM + 10H_2O \xrightarrow{R_{Meth}} 53CH_4 + 43CO_2 + 12NH_4^+ + HPO_4^{2-} \qquad 6)$$
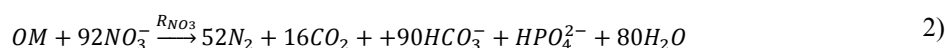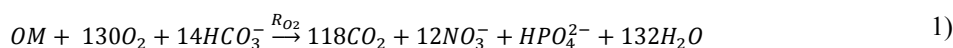
where OM=$(CH_2O)_{106}(NH_3)_{12}HPO_4$, although stoichiometry differs between modelling studies. The models examined here follow Berner's principle of calculating the oxidation of organic matter as a function of OM concentration and usually independent of oxidant concentration while the concentration is high. When the oxidant is reduced to limiting concentrations, a limitation effect is included (Berner, 1964). In addition, reactions with oxidants resulting in a higher free energy yield are assumed to occur in preference to those involving oxidants with lower free energy yield. For example, aerobic bacteria will consume OM until the O_2 is consumed, after which the denitrifying bacteria will be able to oxidise OM at the maximum rate (Megonigal *et al.*, 2003). The models take this process into account by including an inhibition factor in the rate laws.

The models that have been developed adopt different algorithms to represent these chemical and microbial processes (OM dependence, limitation and inhibition) mathematically, while attempting to strike their own balance between simplicity and complexity. The aim of this study was to analyse and compare three common approaches and identify similarities and differences between them. We firstly present the rate laws in equivalent notation to highlight differences and similarities, and secondly we quantitatively assess the differences between the approaches when applied to two hypothetical sediment conditions, representing marine and fresh water.

2. MODEL APPROACHES

Approach 1 originally stems from Boudreau (1996), Approach 2 from Van Cappellen and Wang (1996) and Approach 3 from Soetaert *et al.*(1996a; 1996b). The total OM reaction rate (R_{OM}) is the sum of oxidation pathways (1) to (6) in Approaches 1 and 2 (from Van Cappellen and Wang, 1996), and pathways (1), (2) and (7) in Approach 3, where equation (7) combines several anoxic processes.

$$OM + An\ oxidant \xrightarrow{R_{Anox}} 106ODU + 106CO_2 + 12NO_3^- + HPO_4^{2-} + 106H_2O \qquad 7)$$
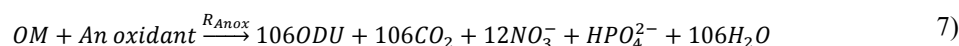
Oxygen demand units (ODU) in Eq.7 are a combination of reduced-species products of anoxic oxidation that could be oxidised by other processes. The governing rate laws have been expressed in Table 1.

Table 1 Summary of the three main approaches to OM oxidation equations

R_{OM} Total OM oxidation rate	Oxidation rate due to i^{th} oxidant R_{Ox_i}	Oxidation term Θ_{Ox_i}	Inhibition term Θ_{In_i} $\Theta_{In_1} = 1$
Approach 1 *i* from reactions 1 to 6 $R_{OM} = \sum_{i=1}^{6} R_{Ox_i}$	$R_{Ox_i} = k_{OM}OM\Theta_{Ox_i}\Theta_{In_i}$	for i = 1 to 5, $\Theta_{Ox_i} = \left(\frac{Ox_i}{K_{Ox_i}+Ox_i}\right)$, $\Theta_{Ox_6} = 1$	for i = 2 to 6, $\Theta_{In_i} = \prod_{j=1}^{i-1}\left(\frac{K_{Ox_j}}{Ox_j+K_{Ox_j}}\right)$
Approach 2 *i* from reactions 1 to 6 $R_{OM} = \sum_{i=1}^{6} R_{Ox}$ $= k_{OM}OM$	for i = 1 to 5 $R_{Ox_i} = k_{OM}OM\Theta_{Ox_i}\Theta_{In_i}$ and $R_{Ox_6} = k_{OM}OM - \sum_{i=1}^{5} R_{Ox_i}$	for i = 1 to 5 $\Theta_{Ox_i} = \begin{cases} 0 & \text{when } Ox_{i-1} > L_{Ox_{i-1}} \\ 1 & \text{when } Ox_{i-1} < L_{Ox_{i-1}} \text{and } Ox_i > L_{Ox_i} \\ \frac{Ox_i}{L_{Ox_i}} & \text{when } Ox_{i-1} < L_{Ox_{i-1}} \text{and } Ox_i < L_{Ox_i} \end{cases}$ $\Theta_{Ox_6} = 1$	for i = 2 to 5 $\Theta_{In_i} = \prod_{j=1}^{i-1}\left(1 - \frac{Ox_j}{L_{Ox_j}}\right)$
Approach 3 *i* from reactions 1, 2 and 7 $R_{OM} = \sum_{i=1}^{3} R_{Ox_i}$	$R_{Ox_i} = k_{OM}OM\Theta_{Ox_i}\Theta_{In_i}$	for i = 1, 2 , $\Theta_{Ox_i} = \frac{\left(\frac{Ox_i}{K_{Ox_i}+Ox_i}\right)}{\left\{\left[\left(\frac{O_2}{K_{O_2}+O_2}\right)+\left(\frac{NO_3}{K_{NO_3}+NO_3}\right)\left(\frac{K_{O_2}^{NO_3}}{O_2+K_{O_2}^{NO_3}}\right)\right] + \left(\frac{K_{NO_3}^{Anox}}{NO_3+K_{NO_3}^{Anox}}\right)\left(\frac{K_{O_2}^{Anox}}{O_2+K_{O_2}^{Anox}}\right)\right\}}$ for i = 3, $\left(\frac{Ox_i}{K_{Ox_i}+Ox_i}\right) = 1$	for i = 2, 3 $\Theta_{In_i} = \prod_{j=1}^{i-1}\left(\frac{K_{In_j}}{Ox_j+K_{In_j}}\right)$ $= \prod_{j=1}^{i-1}\left(1 - \frac{Ox_j}{Ox_j+K_{In_j}}\right)$

Approach 1	Boudreau 1996, Boudreau 1998, Luff et al. 2000, Haeckel et al. 2001, Koenig et al. 2001, Wijsman et al. 2002, Meysman 2003, Luff and Moll 2004, Katsev et al. 2006, Devallois et al. 2008, Dittrich et al. 2009, Massoudieh et al. 2010
Approach 2	Van Cappellen and Wang 1996, Hunter et al. 1998, Berg et al. 2003, Fossing et al. 2004, Canavan et al. 2006, Sochaczewski et al. 2008, Kasih et al. 2008, 2009, Dale et al. 2009
Approach 3	Soetaert et al. 1996a, b, Middelburg et al. 1996, Soetaert 1998, Epping 2002, Sohma et al. 2008, Berg et al. 2007, Hochard et al. 2010

A common feature of all three approaches is that the oxidation expression R_{Ox} is a product of four terms: an OM reaction rate constant k_{OM}; the OM concentration; a term Θ_{Ox} for limitation; and an inhibition term Θ_{In}. In Approach 2 the sum of the individual oxidation pathway fractions always adds to 1 and R_{OM} is always equal to $k_{OM}OM$. This is achieved by setting the rate of methanogenesis, R_{Meth} (the last OM breakdown pathway, equation (6)), to the difference between $k_{OM}OM$ and the sum of the five higher-energy pathways. In contrast, in Approach 1, R_{Meth} has a separate rate expression (Table 1). However, as the concentrations of higher oxidants decrease towards zero, Θ_{Ox} and Θ_{In} tend towards 1 and therefore R_{Meth} in Approach 1 also approaches $k_{OM}OM$.

The Θ_{Ox} term in Approach 1 is a Monod expression, which uses Monod half-saturation constants (K), and which is chosen because it best reflects laboratory data of bacterially-controlled oxidation reactions (Boudreau and Westrich, 1984). The Θ_{Ox} of Approach 3 consists of Monod functions, but also includes inhibition terms. In Approach 2 the Θ_{Ox} is either 0, 1 or the ratio of Ox_i to L_{Ox_i}, depending on the oxidant concentration relative to L_{Ox_i}, the specified limiting concentration.

The inhibition term Θ_{In} in Approaches 1 and 3 is a Monod function, while in Approach 2 it is the 'modified Monod' term, which employs Blackman kinetics (Boudreau, 1997). Approach 3 has separate K_{Ox} and K_{In} values, whereas in the original references for Approaches 1 and 2 it is assumed that the equivalent of a K_{In} or L_{In} term would have the same value as K_{Ox} or L_{Ox}. The value of the L_{Ox} in Approach 2 is a limiting concentration rather than a Monod half-saturation constant and therefore not directly comparable to the half-saturation constants of Approaches 1 and 3, but it serves a similar purpose by limiting the reaction and inhibiting subsequent reactions. Approach 2 also adopts a discrete 'on/off' type formulation, where the rate is zero when the higher-energy oxidant concentration is above its L_{Ox}. The 'modified Monod' term in Approach

2 was chosen by Van Cappellen and Wang because it "increases computational efficiency and yields metabolic rate distributions that, for all practical purposes, are identical to those calculated with the full Monod law" (Van Cappellen and Wang, 1996). Whether these terms are in fact identical is a question that is investigated with the following experiments.

3. MODEL APPLICATION

For each of the three approaches, two simple numerical experiments were carried out where a homogenous unit of sediment was left to react in a closed system with a specified finite initial amount of each oxidant. In the second experiment the initial SO_4^{2-} concentration was much lower, representing conditions of a freshwater lake, with SO_4^{2-} concentrations and constants taken from (Katsev *et al.*, 2006) and (Van Cappellen and Wang, 1995) for Approaches 1 and 2, respectively. All transport processes and other secondary chemical reactions were excluded. The initial concentrations of OM and oxidants in the first experiment were based on values in Boudreau (1996), Van Cappellen and Wang (1995, 1996) and Luff and Moll (2004), for typical coastal marine environments (Table 2). The K_{Ox}, K_{In}, L_{Ox}, and L_{In} values were taken from Boudreau (1996), Van Cappellen and Wang (1996) and Soetaert *et al.* (1996) for Approaches 1, 2 and 3, respectively. The reactions (1) to (6) were used for Approaches 1 and 2 and reactions (1), (2) and (7) for Approach 3, with the stoichiometry from Van Cappellen and Wang (1996). The calculations were run for 3 years with an hourly time step using a first-order explicit finite difference.

Table 2 Initial conditions (μM) and oxidation and inhibition constants

	Initial concentration (μM)						Monod K or limiting concentration L					K_{In} for Approach 3		
	O_2	NO_3	Mn	Fe	SO_4	OM	O_2	NO_3	Mn	Fe	SO_4	K_{O2}^{NO3}	K_{O2}^{Anox}	K_{NO3}^{Anox}
A1							8	30	10000	10000		-	-	-
Marine	231	20	48000	50000	28000	500					1000			
Fresh	231	20	48000	50000	100	500					400			
A2							20	5	24000	150000		-	-	-
Marine	231	20	48000	50000	28000	500					1600			
Fresh	231	20	48000	50000	100	500					300			
A3							3	30	-	-	-	10	5	5
Marine	231	20	-	-	-	500								
Fresh	231	20	-	-	-	500								

4. RESULTS

Changes in oxidant concentrations with time are shown in Figure 1. The total OM oxidation rates and contribution by different oxidation pathways are given in Figure 2. Oxidant exhaustion times, defined as when the oxidant reaches less than 1% of its initial concentration, are given in Table 4.

In Approach 1 R_{O2} began as 96.7% of the total R_{OM}, R_{NO3} 1.3% and R_{Mn} 1.7% and there were very small contributions of the other three pathways. Approach 2 began with oxidation only by O_2, as the inhibition term set the rates of the other pathways to zero. In Approach 3 R_{O2} began as 96.1% of R_{OM}, R_{NO3} as 3.5% and R_{Anox} as 0.4%.

Despite these differences, the exhaustion times of O_2 were similar for all approaches (Table 3). The exhaustion times for NO_3^- were the same in Approaches 2 and 3 but one day later in Approach 1. Using the K_{Ox} and K_{In} values from Soetaert *et al.* (1996a; 1996b), in Approach 3 aerobic inhibition had a much stronger effect on subsequent reactions than that of NO_3^- inhibition on anaerobic processes. As a result, R_{OM} exhibited an increase in the period after O_2 was exhausted and before NO_3^- was exhausted (Figure 2), as denitrification and anoxic processes simultaneously oxidised the OM. With the "on/off" inhibition of Approach 2, the lower-energy oxidation pathways did not start until later and the overlap of pathways seen in Approaches 1 and 3 only occurred when the initial concentrations were below the limiting concentrations. The amounts of the oxidants remaining in Approach 1 at the equivalent start-time of an oxidation pathway in Approach 2 are given in Table 3. As an example, when oxidation by NO_3^- began in Approach 2 on day 1.5, 25% of the NO_3^- in Approach 1 was already consumed. Exhaustion times were similar between the marine and freshwater experiments, as expected given the similar configuration, except that SO_4^{2-} reduction played a much smaller role and methanogenesis a much larger role in freshwater than in the marine experiment. Mn(IV) and Fe(III) were exhausted in Approach 1 but not within the simulation time in Approach 2, given the initial concentrations used here. In the marine experiment, SO_4^{2-} was not exhausted; in the lake experiment, SO_4^{2-} was exhausted 210 days later in Approach 1 than in Approach 2. Of note is that in both approaches where

SO$_4^{2-}$ reduction is considered, SO$_4^{2-}$ was exhausted before Mn(IV) and Fe(III) in the freshwater experiments because of its much lower starting concentrations, despite the inhibition by higher-energy pathways which kept R_{SO4} low.
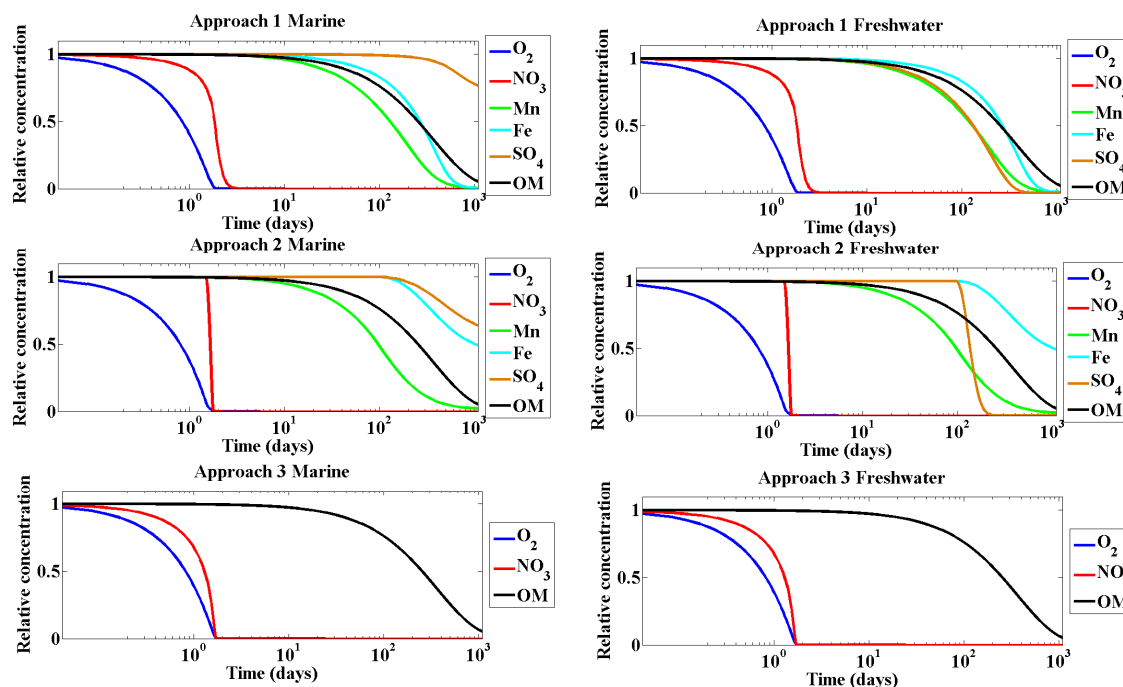

Figure 1 Changes in oxidant concentration with time relative to their initial concentrations.

Table 3 Oxidant in Approach 1 remaining at onset of oxidation pathway in Approach 2
(*NE*= not exhausted)

	O$_2$	NO$_3^-$	Mn(IV)	Fe(III)	SO$_4^{2-}$
A1 Marine	1.83	2.79	797	857	*NE*
Fresh	1.83	2.79	797	857	716
A2 Marine	1.71	1.79	*NE*	*NE*	*NE*
Fresh	1.71	1.79	*NE*	*NE*	*NE*
A3 Marine	1.71	1.71	-	-	-
Fresh	1.71	1.71	-	-	-

Table 4 Oxidant exhaustion times (days)

	O$_2$	NO$_3^-$	Mn(IV)	Fe(III)	SO$_4^{2-}$
A1 % remaining Marine	100	75	100	83	99
Fresh	100	75	100	83	62
A2 Start day	1	1.5	1.75	96.1	96.1

5 DISCUSSION

Despite the different approaches being built on similar conceptual models of sequential redox reactions, the choice of different kinetic expressions results in differences in sediment behaviour. Approach 1 allows all oxidation reactions to occur simultaneously, albeit with strong inhibition of the lower-energy oxidation pathways in the early stages. In Approach 2 the sediment allows for only one oxidation pathway to be active at any significant rate at a given time while the oxidant is above the equivalent L_{Ox}. While Approach 3 is less informative in that it lumps Mn(IV), Fe(III) and SO$_4^{2-}$ reduction into a single anoxic process, its use of separate K_{Ox} and K_{In} gives it separate control of limitation and inhibition. However, despite the very different K_{Ox} values and limitation expressions in the three approaches, there were some surprising similarities, such as the initial reaction pathway profile in Approaches 1 and 3, and the O$_2$ exhaustion times in all approaches. Also of interest was that in both the Approach 1 and 2 freshwater experiments, the expected sequential oxidant depletion of Mn(IV), Fe(III) and SO$_4^{2-}$ was not seen because initial concentrations of Mn(IV) and Fe(III) were high relative to SO$_4^{2-}$. However, in practice, secondary reactions such as reoxidation of S^{2-} to SO$_4^{2-}$ by Fe(III), would likely occur, leading to a higher apparent rate of Fe(II) reduction, and a longer apparent exhaustion time for SO$_4^{2-}$. Furthermore, the Fe and Mn in the sediments may be present in phases of varying lability (e.g. Berg *et al.*, 2003). With these processes included in the model, the differences between

the approaches could be amplified or suppressed. However, it is notable that the rate expressions for primary reactions in both approaches allow depletion of SO_4^{2-} prior to more thermodynamically favourable oxidants.
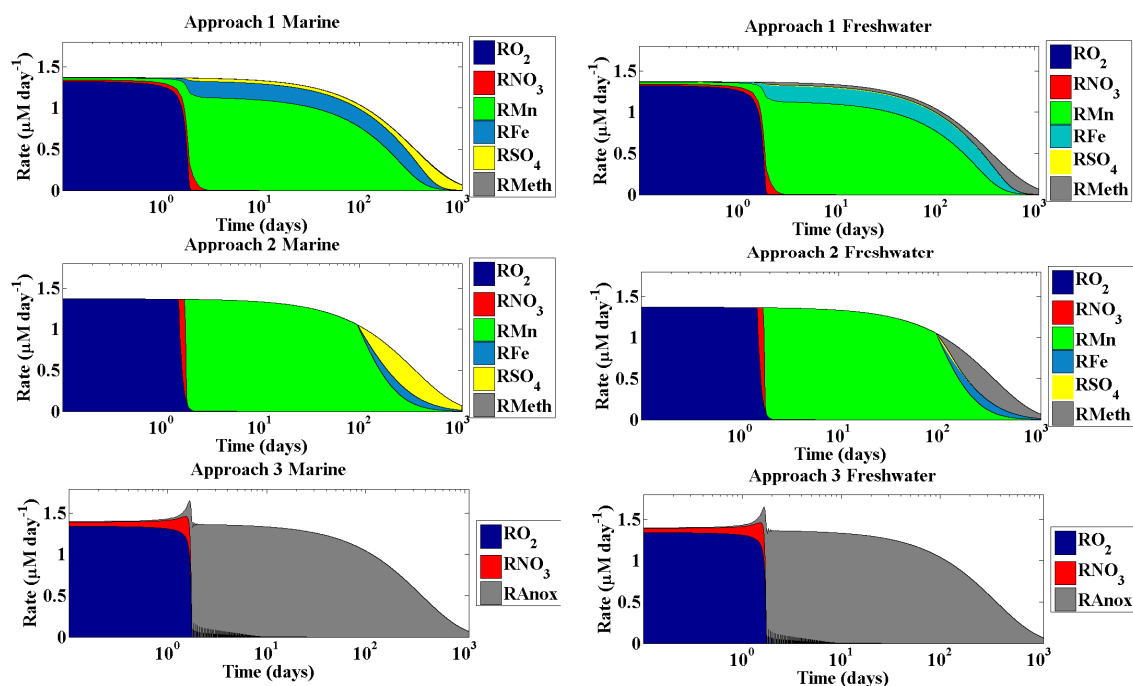
Figure 2 Total organic matter reaction rate and contribution of each oxidation pathway.

The temporal overlap of rates seen in Approach 1 creates a notable difference in the times at which oxidants are consumed compared to Approach 2. While quantities will depend on initial concentrations, in this example 38% of SO_4^{2-} in Approach 1 was consumed before SO_4^{2-} reduction commenced in Approach 2. In the case of Fe(III) reduction, a 17% difference in the generation of the reduced product Fe(II) over 96.1 days would lead to a considerable difference in the rate of diffusion of Fe(II) across sediment model layers.

When considering these OM oxidation reactions alone, the assumption that the Monod functions of Approaches 1 and 3 and Van Cappellen and Wang's "Modified Monod" are "identical" is not correct. The differences in the rate expressions resulted in different temporal evolution of oxidant concentrations in the different approaches. Whether these approaches are in fact "identical for practical purposes" will be determined in future work that will expand the experiment to a more complex diagenesis model able to account for additional processes as included in the original models, such as secondary chemical reactions and transport processes. Comparison of future laboratory experiments of OM oxidation by this series of oxidants may be able to show which approaches are the most appropriate for different environmental conditions.

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