Bottom RedOx Model (BROM, v.1.1): a coupled benthic pelagic model for simulation of water and sediment biogeochemistry

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15 Abstract. Interactions between seawater and benthic systems play an important role in global biogeochemical

- 16 cycling. Benthic fluxes of some chemical elements (e.g. C, N, P, O, Si, Fe, Mn, S) alter the redox state and
- 17 marine carbonate system (i.e. pH and carbonate saturation state), which in turn modulate the functioning of
- 18 benthic and pelagic ecosystems. The redox state of the near bottom layer in many regions can change with time,
- 19 responding to the supply of organic matter, physical regime and coastal discharge. We developed a model
- 20 (BROM) to represent key biogeochemical processes in the water and sediments and to simulate changes
- 21 occurring in the bottom boundary layer. BROM consists of a transport module (BROM-transport) and several
- 22 biogeochemical modules that are fully compatible with the Framework for the Aquatic Biogeochemical Models,
- allowing independent coupling to hydrophysical models in 1D, 2D or 3D. We demonstrate that BROM is
- 24 capable of simulating the seasonality in production and mineralization of organic matter as well as the mixing
- that leads to variations in redox conditions. BROM can be used for analyzing and interpreting data on sediment-
- 26 water exchange, and for simulating the consequences of forcings such as climate change, external nutrient
- 27 loading, ocean acidification, carbon storage leakage, and point-source metal pollution.
- 28 Key Words modeling; Bottom Boundary Layer; benthic fluxes; nutrient cycles; anoxic conditions; carbonate system.
- 29

30 1 Background

Oxygen depletion and anoxia are increasingly common phenomena observed in the World Ocean, inland seas and coastal areas. Observations show a decline in dissolved oxygen concentrations at continental margins in many regions and this has been linked to both an increase in anthropogenic nutrient loadings and a decrease in vertical mixing e.g. (Diaz and Rosenberg, 2008; Rabalais et al., 2002; Richardson and Jørgensen, 1996). Although bottom waters may be permanently oxic or anoxic, they oscillate seasonally between these extremes in 1 many water bodies (Morse and Eldridge, 2007). Such oscillations typically result from variations in the supply of

2 organic matter (OM) to the sediment-water interface (SWI), from the hydrophysical regime (mixing/ventilation),

3 and from nutrient supply (river run-off). Frequently, oxic conditions during periods of intense mixing are

4 followed by near-bottom suboxia or anoxia after the seasonal pycnocline forms, restricting aeration of the deeper

5 layers. This occurs for instance on the Louisiana shelf (Morse and Eldridge, 2007; Yu et al., 2015) and in

6 Corpus Christi Bay (McCarthy et al., 2008), the Sea of Azov (Debolskaya et al., 2008), and Elefsis Bay

7 (Pavlidou et al., 2013).

8 The redox state and oxygenation of near-bottom water varies due to the transport of oxidized and reduced 9 species across the SWI and biogeochemical processes occurring in the sediments (Cooper and Morse, 1996; 10 Jorgensen et al., 1990; Roden and Tuttle, 1992; Sell and Morse, 2006). The sediments generally consume 11 oxygen due to the deposition of labile OM and the presence of reduced forms of chemical elements. Their 12 capacity to exchange oxygen with the pelagic layer is limited, as near bottom water is usually characterized by 13 low water velocity and reduced mixing in the vicinity of the SWI (Glud, 2008). In some cases, a high benthic 14 oxygen demand (BOD) associated with local OM mineralization and low mixing rates can cause anoxia in the 15 bottom water. This may lead to death, migration, or changed behavior of the benthic macro and meio faunal 16 organisms responsible for bioturbation and bioirrigation (Blackwelder et al., 1996; Sen Gupta et al., 1996; Morse 17 and Eldridge, 2007), which in turn can greatly slow down the transport of solid and dissolved species inside the 18 sediments and therefore the rates of oxidative reactions. Under such conditions, sedimentary sulfides can build 19 up, and dissolution of carbonate minerals may come to a halt (Morse and Eldridge, 2007). When oxic conditions 20 return, there can be an "oxygen debt" of reduced species in the water column (Yakushev et al., 2011) which may

21 buffer and delay reoxygenation of the sediments (Morse and Eldridge, 2007).

22 In areas experiencing seasonal hypoxia/anoxia the processes taking place in the water column and in the 23 sediments are tightly coupled to each other, as well as to the fluxes and exchanges of organic matter over a range 24 of time scales. An accurate understanding of physical, chemical, and biological processes driving changes in 25 redox conditions is needed to predict the distribution of hypoxia/anoxia in a given environment. This "benthic-26 pelagic coupling" broadly encompasses the fluxes of OM to the sediments and the return fluxes of inorganic 27 nutrients to the water column. Variations in supply, dynamics and reactivity of OM affect benthic communities 28 (Pearson and Rosenberg, 1978), sediment and porewater geochemistry (Berner, 1980), and nutrient and oxygen 29 fluxes at the SWI (Boudreau, 1997).

30 Many previous studies have demonstrated the capability of sophisticated reactive transport codes for integrated 31

32 al., 2010; Jourabchi et al., 2005; Katsev et al., 2006, 2007; Paraska et al., 2014; Soetaert et al., 1996). The water

modelling of biogeochemical cycles in sediments (Boudreau, 1996; Van Cappellen and Wang, 1996; Couture et

33 column redox interface was also specifically targeted in the models of (Konovalov et al., 2006; Yakushev et al.,

34 2006, 2007). However, the process of integrating such models with pelagic biogeochemical models to produce

35 benthic-pelagic coupled models has only begun in recent years.

As of the year 2000, benthic-pelagic coupling was either neglected or crudely approximated in many pelagic 36

37 biogeochemical and early diagenetic models (Soetaert et al., 2000). One of the first fully coupled physical-

38 pelagic-benthic biogeochemical modes was developed for the Goban Spur shelf-break area to examine the

- 1 impact of in-situ atmospheric conditions on ecosystem dynamics, to understand biogeochemical distributions in
- 2 the water column and the sediments, and to derive a nitrogen budget for the area. This model was most suited to
- 3 testing the impact of short-term physical forcing on the ecosystem (Soetaert et al., 2001).
- 4 Later, several coupled benthic-pelagic models were produced with an emphasis on studying eutrophication 5 (Cerco et al., 2006; Fennel et al., 2011; Soetaert and Middelburg, 2009) or hypoxia in various locations
- 6 including Tokyo bay (Sohma et al., 2008), the Baltic Sea (Reed et al., 2011), the North Sea Oyster Grounds
- 7 (Meire et al., 2013) and Southern Bight (Lancelot et al., 2005). Another model was created to investigate early
- 8 diagenesis of silica in the Scheldt estuary, with benthic-pelagic coupling only of silica (Arndt and Regnier,
 9 2007).
- 10 By coupling two quite sophisticated models ECOHAM1 and C.CANDI, a 3D model for the North Sea was 11 created where pelagic model output was used to force a benthic biogeochemical module (Luff and Moll, 2004). 12 Another physical-biological model for the North Sea, PROWQM, is more complex than ECOHAM1 and has 13 been coupled to a benthic module to simulate seasonal changes of chlorophyll, nutrients and oxygen at the 14 PROVESS north site, south-east of the Shetland Islands (Lee et al., 2002). (Brigolin et al., 2011) developed a 15 spatially explicit model for the northwestern Adriatic coastal zone by coupling a 1D transient early diagenesis 16 model with a 2D reaction-transport pelagic biogeochemical model. Currently, the most known and established 17 coupled model is ERSEM - the European Regional Seas Ecosystem Model that was initially developed as a 18 coastal ecosystem model for the North Sea and which has evolved into a generic tool for ecosystem simulations
- 19 from shelf seas to the global ocean (Butenschön et al., 2016).
- 20 The BROM model described herein is a fully coupled benthic-pelagic model with a special focus on 21 deoxygenation and redox biogeochemistry in the sediments and Benthic Boundary Layer (BBL). The BBL is 22 "the part of the marine environment that is directly influenced by the presence of the interface between the bed 23 and its overlying water" (Dade et al., 2001). Physical scientists tend to prefer the term "bottom boundary layer", 24 but this is largely synonymous with the BBL (Thorpe, 2005). Within BROM, the term BBL refers to the lower 25 parts of the fluid bottom boundary layer where bottom friction strongly inhibits current speed and vertical 26 mixing, hence including the viscous and logarithmic sublayers up to at most a few meters above the sediment. This calm-water layer plays a critical role in mediating the interaction of the water column and sediment 27 28 biogeochemistry and in determining e.g. near-bottom oxygen levels, yet it remains poorly resolved in most physical circulation models. For BROM we have developed an accompanying offline transport module 29 "BROM-transport" that uses output from hydrodynamic water column models but solves the transport-reaction 30 31 equations for a "full" grid including both water column and sediments. BROM-transport uses greatly increased
- 32 spatial resolution near to the SWI, and thereby provides explicit spatial resolution of the BBL and sediments.
- 33 The goal of this work was to develop a model that captures key biogeochemical processes in the water and
- 34 sediment and to analyze the changes occurring in the BBL and SWI. As a result, BROM differs from existing
- 35 biogeochemical models in several key respects. BROM features explicit, detailed descriptions of many chemical
- 36 transformations under different redox conditions, and tracks the fate of several chemical elements (Mn, Fe, and
- S) and compounds (MnCO₃, FeS, S0, S_2O_3) that rarely appear in other models. BROM also allows for spatially
- 38 explicit representations of the vertical structure in the sediments and BBL. This distinguishes it from e.g.

1 ERSEM (Butenschön et al., 2016), which has a more detailed representation of larger benthic organisms 2 (meiofauna and different types of macrofauna), but limits its chemistry to the dissolved phase to CO₂, O₂ and 3 macronutrients, its benthic bacteria to two functional groups, and its sedimentary vertical structure to an implicit 4 three-layer representation that relies on equilibrium profiles of solutes and idealized profiles of particulates. 5 Third, BROM offers a near-comprehensive representation of all processes affecting oxygen levels in the BBL 6 and sediments, and should therefore provide a useful tool for studies focused on deoxygenation in deep water 7 and sediments. Finally, BROM is designed as a flexible model that can be applied in a broad range of marine 8 and lake environments and modelling problems. As a component of the Framework for Aquatic Biogeochemical 9 Modelling (FABM, Bruggeman and Bolding, 2014), BROM can be very easily coupled online to any 10 hydrodynamic model within FABM, and can also be driven offline by hydrodynamic model output saved in 11 NetCDF or text format using the purpose-built offline transport solver BROM-transport.

12 2 BROM description

BROM consists of two modules, BROM-biogeochemistry and BROM-transport. BROM-biogeochemistry builds 13 14 on ROLM (RedOx Layer Model), a model constructed to simulate basic biogeochemical structure of the water column oxic/anoxic interface in the Black Sea, Baltic Sea, and Norwegian fjords (He et al., 2012; Stanev et al., 15 16 2014; Yakushev et al., 2009, 2006, 2007, 2011). In BROM-biogeochemistry we extended the list of modelled 17 compounds and processes (Figure 1). BROM considers interconnected transformations of species of (N, P, Si, C, 18 O, S, Mn, Fe) and resolves OM in nitrogen currency. OM dynamics include parameterizations of OM production 19 (via photosynthesis and chemosynthesis) and OM decay via oxic mineralization, denitrification, metal reduction, 20 sulfate reduction and methanogenesis. To provide a detailed representation of changing redox conditions, OM in 21 BROM is mineralized by several different electron acceptors and dissolved oxygen is consumed during both 22 mineralization of OM and oxidation of various reduced compounds. Process inhibition in accordance with redox 23 potential is parameterized by various redox-dependent switches. BROM also includes a module describing the 24 carbonate equilibria; this allows BROM to be used to investigate acidification and impacts of changing pH and 25 saturation states on water and sediment biogeochemistry.

The physical domain of BROM-transport spans the water column, BBL and upper layers of the sediments in a continuous fashion. This allows for an explicit, high-resolution representation of the BBL and upper sediments, while also allowing the boundary conditions to be moved as far as possible from these foci of interest i.e. to the air-sea interface and to deep in the sediment.

- BROM is integrated into an existing modular platform (FABM) and is therefore coded as a set of reusable "legobrick" components, including the offline transport driver BROM-transport and modules for ecology, redox chemistry, and carbonate chemistry. This means that BROM-transport can be used with all biogeochemical modules available in FABM, including e.g. the modules comprising ERSEM, and that BROM biogeochemical modules can be used in all other 1D and 3D hydrodynamic models supported by FABM (e.g., GOTM, GETM, MOM5, NEMO, FVCOM). Individual BROM modules can also be coupled to existing ecological models to
- 36 expand their scope, e.g. by providing descriptions of redox and carbonate chemistry. Using the FABM

1 framework thus facilitates the transparent and consistent setup of complex biogeochemical reaction networks for

2 the prediction of hypoxia/anoxia while harnessing the capabilities of various hydrophysical drivers.

3 2.1 Biogeochemical module

4 2.1.1 General description

5 BROM-biogeochemistry consists of 3 biogeochemical submodules: BROM_bio (ecological model), 6 BROM redox (redox processes) and BROM carb (carbonate system). Interactions between modelled variables 7 are either kinetic (e.g. OM degradation) or equilibrium processes (e.g. carbonate system equilibration) 8 (Boudreau, 1996; Jourabchi et al., 2008; Luff et al., 2001). In general, the redox reactions are fast in comparison 9 with the other processes and a typical model time step. Species involved in such reactions are therefore set to 10 equilibrium concentrations using mass action laws and equilibrium constants for seawater (Millero, 1995). Total 11 scale pH is also diagnosed at every time step, mainly as a function of dissolved inorganic carbon (DIC) and total 12 alkalinity (Alk) which are both prognostic (state) variables.

13 The model has 33 state variables (Table 1), including frequently measured components such as hydrogen sulfide 14 (H_2S) and phosphate (PO₄), as well as rarely measured variables such as elemental sulfur (S⁰), thiosulfate (S₂O₃), trivalent manganese species Mn(III), and bacteria. We acknowledge that for many of these, site-specific 15 16 estimates of associated model parameters and initial/boundary conditions may be difficult or impossible to 17 obtain, and may in practice require some crude assumptions and approximations (e.g. universal default parameter 18 values, no-flux boundary conditions, initial conditions from a steady annual cycle). Nevertheless, we believe 19 that for many applications this caveat will be acceptable given the additional process resolution and realism 20 provided by BROM for important biogeochemical processes in the BBL and sediments. The equations and 21 parameters employed in BROM are given in Tables 2 and 3, and a flow chart is shown in Figure 1. 22

1

2 2.1.2 Ecosystem and redox models

3 The overall goal of the ecosystem representation is to parameterize the key features of OM production and 4 decomposition, following Redfield and Richards stoichiometry (Richards, 1965). We divide all the living OM 5 (biota) into Phy (photosynthetic biota), Het (non-microbial heterotrophic biota), and 4 groups of "bacteria" 6 which may be considered to include microbial fungi. These latter are: Baae (aerobic chemoautotrophic bacteria), 7 Baan (anaerobic chemoautotrophic bacteria), Bhae (aerobic heterotrophic bacteria), and Bhan (anaerobic 8 heterotrophic bacteria). OM is produced photosynthetically by Phy and chemosynthetically by bacteria, 9 specifically by Baae in oxic conditions and by Baan in anoxic conditions. Growth of heterotrophic bacteria is 10 tied to mineralization of OM, favouring Bhae in oxic conditions and Bhan in anoxic conditions. Secondary 11 production is represented by Het which consumes phytoplankton as well as all types of bacteria and dead 12 particulate organic matter (detritus, which is also explicitly modelled). The effect of suboxia and anoxia is 13 parameterized by letting the mortality of aerobic organisms depend on the oxygen availability.

14 A detailed account of processes representing the inorganic cycling of (N, S, Mn, Fe, P) is given in the description 15 of ROLM (Yakushev et al., 2007, 2013a), while the process parametrization, chemical reactions, rates and 16 stoichiometric constants values are summarized in Tables 2-4. Table 2 also describes the redox-dependent 17 switches, nutrient limitation, and substrate consumption rates for heterotrophs. The redox-dependent switches 18 are mostly based on hyperbolic tangent functions which improve system stability compared with discrete 19 switches. The nutrient limitation and heterotrophic transfer functions are based on squared Monod laws for 20 Nutrient/Biomass ratio, which also stabilizes the system compared with Michaelis-Menten and Ivlev 21 formulations. Here we describe the parameterization of carbon that was not considered in ROLM and was not 22 described in (Yakushev, 2013).

23 2.1.3 Total alkalinity

Total alkalinity, A_T , is a model state variable. Following the formal definition of A_T (Dickson, 1992; Wolf-Gladrow et al., 2007; Zeebe and Wolf-Gladrow, 2001) the following alkalinity components were considered:

26 $A_T = A_{TCO2} + A_B + A_{TPO4} + A_{Si} + A_{NH3} + A_{H2S} + [OH^-] - A_{SO4} - A_{HF} - A_{HNO3} - [H^+]$

27 where the carbonate alkalinity $A_{TCO2} = [HCO_3^-] + 2[CO_3^2-]$, phosphoric alkalinity $A_{TPO4} = [HPO_4^{2-}] + 2[PO_4^{3-}] - 2[PO_$

28 $[H_3PO_4]$, silicic alkalinity $A_{Si} = [H_3SiO_4]$, ammonia alkalinity $A_{NH3} = [NH_3]$, and hydrogen sulfide alkalinity A_{H2S}

- 29 =[HS⁻] were calculated from the corresponding model state variables (Table 1) according to (Luff et al., 2001;
- 30 Volkov, 1984). The boric alkalinity $A_B = [B(OH)_4]$ was estimated from total dissolved boron which in turn was
- 31 calculated from salinity. $[OH^{-}]$ and $[H^{+}]$ were calculated using the ion product of water (Millero, 1995). The
- 32 hydrogen sulfate alkalinity $A_{SO4} = [HSO_4^-]$, hydrofluoric alkalinity $A_{HF} = [HF]$, and nitrous acid alkalinity A_{HNO3}
- $33 = [HNO_2]$ were ignored due to their insignificant impact on A_T variations in most natural marine and freshwater
- 34 systems.

- 1 Biogeochemical processes can lead to either increase or decrease of alkalinity, and alkalinity can be used as an
- 2 indicator of specific biogeochemical processes (Soetaert et al., 2007). Organic matter production can affect
- 3 alkalinity via the 'nutrient-H⁺ compensating principle' formulated by Wolf-Gladrow et al. (2007): during uptake
- 4 or release of charged nutrient species, electroneutrality is maintained by consumption or production of a proton
- 5 (i.e. during uptake of nitrate for photosynthesis or denitrification, or production of nitrate by nitrification).

6 BROM also considers the effect on alkalinity of the following redox reactions occurring in suboxic and anoxic 7 conditions via production or consumption of $[OH^-]$ and $[H^+]$ and changes in other "standard" alkalinity 8 components A_{TCO2} and A_{H2S} (see bold font):

- 9 $4Mn^{2+} + O_2 + 4H^+ \rightarrow 4Mn^{3+} + 2H_2O$
- $10 \qquad 2Mn^{3+} + 3H_2O + 0.5O_2 \rightarrow 2MnO_2 + 6H^+$
- 11 $2MnO_2 + 7H^+ + HS^- \rightarrow 2Mn^{3+} + 4H_2O + S^0$
- 12 $2Mn^{3+} + HS^- \rightarrow 2Mn^{2+} + S^0 + H^+$
- 13 $Mn^{2+} + HS^- \leftrightarrow MnS + H^+$
- 14 $Mn^{2+}+CO_3^{2-}\leftrightarrow MnCO_3$
- 15 $2 MnCO_3 + O_2 + 2H_2O \rightarrow 2MnO_2 + 2HCO_3 + 2H^+$
- 16 $4Fe^{2+} + O_2 + 10H_2O \rightarrow Fe(OH)_3 + 8H^+$
- 17 $2Fe^{2+} + MnO_2 + 4H_2O \rightarrow Fe(OH)_3 + Mn^{2+} + 2H^+$
- 18 $2Fe(OH)_3 + HS^{\bullet} + 5H^{+} \rightarrow 2Fe^{2+} + S^{0} + 6H_2O$
- 19 $Fe^{2+} + HS^- \leftrightarrow FeS + H^+$
- 20 $FeS + 2.25O_2 + 2.5H_2O \rightarrow Fe(OH)_3 + 2H^+ + SO_4^{2-}$
- 21 $FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$
- 22 $Fe^{2+}+CO_3^{2-}\leftrightarrow FeCO_3$
- $23 \qquad NH_4^+ + 1.5O_2 \rightarrow NO_2^- + 2H^+ + H_2O$
- 24 $0.75CH_2O + H^+ + NO_2^- \rightarrow 0.5N_2 + 1.25H_2O + 0.75CO_2$
- 25 $4S^0 + 3H_2O \rightarrow 2H_2S + S_2O_3^{2-} + 2H^+$
- 26 $2S^0 + O_2 + H_2O \rightarrow S_2O_3^{2-} + 2H^+$
- 27 $4S^0 + 3NO_3 + 7H_2O \rightarrow 4SO_4^2 + 3NH_4 + 2H^4$
- 28 $S_2O_3^{2-} + 2O_2 + 2OH \rightarrow 2SO_4^{2-} + H_2O$
- 29 $5H_2S + 8NO_3 + 2OH \rightarrow 5SO_4^2 + 4N_2 + 6H_2O$
- $30 \qquad Ca^{2+} + CO_3^2 \leftrightarrow CaCO_3$
- 31 Standard alkalinity components were also affected by other reactions considered in the model (see Table 2).

32 2.1.4 Carbonate system

33 Equilibration of the carbonate system was considered as a fast process occurring within seconds (Zeebe and

- 34 Wolf-Gladrow, 2001). Accordingly, the equilibrium solution was calculated at every time step using an iterative
- 35 procedure. The carbonate system was described using standard approaches (Lewis and Wallace, 1998;

- 1 Munhoven, 2013; Roy et al., 1993; Wanninkhof, 2014; Wolf-Gladrow et al., 2007; Zeebe and Wolf-Gladrow,
- 2 2001). The set of constants of (Roy et al., 1993) was used for carbonic acid. Constants for boric, hydrofluoric,
- 3 and hydrogen sulfate alkalinity were calculated according to (Dickson, 1992), for silicic alkalinity according to
- 4 (Millero, 1995), for ammonia alkalinity according to (Luff et al., 2001), and for hydrogen sulfide alkalinity
- 5 according to (Luff et al., 2001) and (Volkov, 1984). The ion product of water was calculated according to
- 6 (Millero, 1995). Total scale pH was calculated using the Newton-Raphson method with the modifications
- 7 proposed in (Munhoven, 2013). Precipitation and dissolution of calcium carbonate were modelled following the
- 8 approach of (Luff et al., 2001) (Table 2).

9 2.2 Physical environment

BROM-biogeochemistry can be coupled online with various hydrodynamic models using FABM, but this may require extensive adaptation of the hydrodynamic model to resolve the BBL and upper sediments. We have therefore developed a simple 1D offline transport-reaction model, BROM-transport, whose model domain spans the water column, BBL, and upper layers of the sediments, with enhanced spatial resolution in the BBL and sediments. All options and parameter values for BROM-transport are specified in a run-time input file brom.yaml. A step-by-step guide to running BROM-transport is provided in Appendix A.

16 2.2.1 BROM-transport model formulation

17 The time space evolution of state variables in BROM-transport is described by a system of 1D transport-reaction 18 equations in Cartesian coordinates. In the water column the dynamics are:

$$19 \qquad \frac{\partial \hat{c}_i}{\partial t} = \frac{\partial}{\partial z} D \frac{\partial \hat{c}_i}{\partial z} - \frac{\partial}{\partial z} v_i \hat{c}_i + \varepsilon_h (\hat{c}_{0i} - \hat{c}_i) + T_{birr(i)} + R_i$$
(1)

where \hat{C}_i is the concentration in units [mmol/m³ total volume] of the *i*th state variable, D(z,t) is the vertical 20 21 diffusivity, v_i is the settling or sinking velocity, $\varepsilon_h(z,t)$ is a rate of horizontal mixing with an external 22 concentration $\hat{C}_{0i}(z,t)$ (or alternatively, a restoring rate to a climatological concentration), $T_{birr(i)}$ is a tendency 23 due to bioirrigation (only non-zero for dissolved substances in the bottom layer of the water column, see below), and R_i is the combined sources-minus-sinks (in this study provided by BROM-biogeochemistry, but in principle 24 25 any biogeochemical model in FABM could be used). Values for D, ε_h , \hat{C}_{0i} , and other forcings used by R_i are 26 configured at run time through input files (see section 2.2.7). Sinking velocities v_i are non-zero only for 27 particulate (non-dissolved) variables and are determined at each time step by the biogeochemical module 28 (through FABM). BROM-biogeochemistry assumes constant sinking velocities for phytoplankton, zooplankton,

- 29 bacteria, detritus, and inorganic particles (Table 3.5).
- 30 In the sediments, dissolved substances or solutes obey the dynamics:

31
$$\varphi \frac{\partial C_i}{\partial t} = \frac{\partial}{\partial z} \varphi D_C \frac{\partial C_i}{\partial z} - \frac{\partial}{\partial z} \varphi u C_i + T_{birrC(i)} + R_i$$
(2)

- 32 where φ is the porosity, assumed constant in time, D_C is the total solute diffusivity, u is the solute burial velocity,
- and C_i is the porewater concentration in units [mmol/m³ porewater]. Particulate substances become part of the
- 34 solid matrix in the sediments. These obey:

35
$$(1-\varphi)\frac{\partial B_i}{\partial t} = \frac{\partial}{\partial z}(1-\varphi)D_B\frac{\partial B_i}{\partial z} - \frac{\partial}{\partial z}(1-\varphi)wB_i + R_i$$
 (3)

- 1 where D_B is the particulate (bioturbation) diffusivity, w is the particulate burial velocity, and B_i is the particulate
- 2 concentration in units [mmol/m³ total solids].
- 3 The porosity $\varphi(z)$ in (2) and (3) is prescribed as an exponential decay, following (Soetaert et al., 1996):

4
$$\varphi = \varphi_{\infty} + (\varphi_0 - \varphi_{\infty})e^{-\frac{(z-z_{SWI})}{\delta}}$$

5 where φ_{∞} is the deep (compacted) porosity, φ_0 is the sediment surface porosity, z_{SWI} is the depth of the SWI, and

(4)

- 6 δ is a decay scale defining the rate of compaction.
- 7 Diffusion within the sediments is assumed to be strictly "intraphase" (Boudreau, 1997), hence the Fickian 8 gradients in (2) and (3) are formed using the concentration per unit volume porewater for solutes and per unit 9 volume total solids for particulates. The total solute diffusivity $D_C = D_m + D_B$, where D_m is the apparent 10 molecular/ionic diffusivity and D_B is the bioturbation diffusivity due to animal movement and 11 ingestion/excretion. The apparent molecular diffusivity $D_m(z) = \theta^{-2} D_0 \frac{\mu_0}{\mu_{SW}}$ is derived from the infinite-dilution molecular diffusivity D_0 (an input parameter) assuming a constant relative dynamic viscosity $\frac{\mu_0}{\mu_{SW}}$ (default value 12 0.94, cf. (Boudreau, 1997), Table 4.10) and a tortuosity parameterized as: $\theta^2 = 1 - 2 \ln \varphi$ from (Boudreau, 13 14 1997), Eqn. 4.120). The bioturbation diffusivity $D_B(z,t)$ is modelled as a Michaelis-Menten function of the 15 dissolved oxygen concentration in the bottom layer of the water column:

16
$$D_B(z,t) = D_{Bmax}(z) \frac{O_{2s}}{O_{2s} + K_{O2s}}$$
 (5)

where $D_{Bmax}(z)$ is a constant over a fixed mixed layer depth in the surface sediments then decays to zero with increasing depth, and K_{O2s} is a half-saturation constant. The rationale for (5) is that the benthic animals that cause bioturbation require a source of oxygen at the sediment surface for respiration.

- 20 Diffusion between the sediments and water column, i.e. across the SWI, raises a subtle issue in regard to 21 particulates. Here any diffusive flux cannot be strictly intraphase, because particulates are modelled as 22 [mmol/m³ total solids] in the sediments but as [mmol/m³ total volume] in the water column. In BROM-23 transport, the bottom layer of the water column is considered a "fluff layer"; particles enter through the upper 24 interface at their sinking velocity and leave through the sediment-water interface (SWI) at the particulate burial 25 velocity. It follows that a portion of the particulate matter in the fluff layer must be considered as settled fluff, 26 but that portion is not predicted by the model. BROM-transport therefore offers two approaches. In the first 27 approach, the bioturbation diffusivity is set to zero on the SWI, so that only solutes can diffuse across the SWI 28 by molecular diffusion. Since the present version of BROM-transport does not parameterize resuspension 29 through the SWI due to fluid turbulence, the SWI thus becomes a one-way street for particulate matter, whose 30 components can only reenter the water column after dissolution. In the second approach, the bioturbation 31 diffusivity is given by (5) on the SWI, but the bioturbation flux is interphase, mixing concentrations in units 32 [mmol/m³ total volume] for both solutes and particulates. This approach is appropriate if bioturbation can be 33 assumed to exchange fluff and sediment, or if it contributes significantly to particulate resuspension.
- The burial velocities u and w in (2) and (3) can be inferred from the porosity profile under the assumptions of steady state compaction (φ constant in time) and no externally-impressed porewater flow (Berner, 1971, 1980; Boudreau, 1997; Meysman et al., 2005). Here, BROM-transport again offers two approaches. In the first approach, the reactions of particles in the sediments are assumed to have negligible impact on the volume

1 fraction of total solids, and the deep particulate burial velocity w_{∞} in compacted sediments (where $\varphi = \varphi_{\infty}$) is

assumed to be a known constant $w_{b\infty}$ (an input parameter). Since compaction ceases at this (possibly infinite) depth, the solute burial velocity must here equal the particulate burial velocity ($u_{\infty} = w_{b\infty}$). Steady state then implies the following burial velocities (Appendix B):

5
$$W = \frac{(1-\varphi_{\infty})}{(1-\varphi)} W_{b\infty} - \frac{1}{(1-\varphi)} D_B^{inter} \frac{\partial \varphi}{\partial z}$$
(6)

$$6 \qquad u = \frac{\varphi_{\infty}}{\varphi} w_{b\infty} + \frac{1}{\varphi} D_B^{inter} \frac{\partial \varphi}{\partial z} \tag{7}$$

where D_B^{inter} is the interphase bioturbation diffusivity, non-zero only at the SWI and only if bioturbation across the SWI is enabled. In the second approach, the reactions of the modelled particulate substances in the sediments modify the total solid volume fraction, and the modelled sinking fluxes from the water column modify the flux of solid volume at the SWI. The velocities in (6, 7) then define background velocities (w_b , u_b) due to non-modelled particulates. Assuming steady state compaction leads to the following corrections to the background burial velocities (see Appendix B):

13
$$w' = \frac{1}{(1-\varphi)} \sum_{i}^{N_p} \frac{1}{\rho_i} \Big[v_{f(i)} \hat{C}_{sf(i)} + \int_{z_{SWI}}^{z} R_i(z') dz' \Big]$$
(8)

14
$$u' = \frac{1}{\varphi} (w'_{\infty} - (1 - \varphi)w')$$
 (9)

where $w' = w - w_b$, $u' = u - u_b$, N_p is the number of particulate variables, ρ_i is the density of the *i*th particle 15 type, $v_{f(i)}$ is the sinking velocity in the fluff layer, $\hat{C}_{sf(i)}$ is the suspended particulate concentration in the fluff 16 layer, R_i is the particulate reaction term, and w'_{∞} is the correction to the deep particulate burial velocity, in 17 18 practice approximated by the deepest value of w'. Since the suspended portion $\hat{C}_{sf(i)}$ is not explicitly modelled, 19 it is approximated as the minimum of the particulate concentrations in the fluff layer and the layer immediately 20 above. In our applications we have found that (8) and (9) can improve the realism of sediment organic matter 21 distributions, mainly by increasing the burial rate following pelagic production and export events such as the 22 spring bloom.

Finally, the process of bioirrigation, whereby benthic organisms flush out their burrows with water from the
sediment surface, is modelled as a non-local solute exchange following (Aller, 2001; Meile et al., 2001; Rutgers
Van Der Loeff and Boudreau, 1997; Schlüter et al., 2000):

26
$$T_{birrC(i)} = \alpha \varphi \frac{o_{2s}}{o_{2s} + K_{O2s}} \left(\hat{C}_{f(i)} - C_i \right) \quad \text{(for solutes)}$$
(10)

where $\alpha(z)$ is the bioirrigation rate in oxic conditions, $\hat{C}_{f(i)}$ is the flushing concentration of solute in the fluff layer, and the Michaelis-Menten function again accounts for the suppression of worm activity in anoxic conditions. The oxic bioirrigation rate $\alpha(z)$ is parameterized as an exponential decay from the sediment surface as in Schlüter et al. (2000). The total mass transfer to/from the sediment column must be balanced by a flux into/out of the fluff layer (see equation (1)):

1
$$T_{birr(i)} = \frac{1}{h_f} \frac{O_{2S}}{O_{2S} + K_{O2S}} \int_{z_{SWI}}^{z_{max}} \alpha \varphi \left(C_i - \hat{C}_{f(i)} \right) dz' \quad \text{(for solutes)}$$
(11)

where h_f is the thickness of the fluff layer and z_{max} is the depth of the bottom of the modelled sediment column. $T_{birrC(i)}, T_{birr(i)} = 0$ for all particulate variables.

4 2.2.2 BROM-transport numerical integration

5 Equations (1-3) are integrated numerically over a single combined grid (water column plus sediments) and using 6 the same model time step in both water column and sediments. All concentrations are stored internally and 7 input/output in units [mmol/m³ total volume]. Time stepping follows an operator splitting approach (Butenschön 8 et al., 2012): concentrations are successively updated by contributions over one time step of diffusion, 9 bioirrigation, reaction, and sedimentation, in that order. If any state variable has any 'not-a-number' values at the 10 end of the time step then the program is terminated.

- 11 Diffusive updates are calculated either by a simple forward-time central-space (FTCS) algorithm or by a semi-12 implicit, central-space algorithm adapted from a routine in the General Ocean Turbulence Model, GOTM 13 (Umlauf et al., 2005). Bioirrigation and reaction updates are calculated from forward Euler time steps, using 14 FABM to compute R_i , and sedimentation updates are calculated using a simple first-order upwind differencing 15 scheme. After each update, Dirichlet boundary conditions (see below) are reimposed and all concentrations are low-bounded by a minimum value (default = $10^{-11} \mu M$) to avoid negative values. Maximum diffusive and 16 17 advective Courant numbers can optionally be output after every time step or when/if a 'not-a-number' value is detected. Before starting the integration, the program calculates Courant numbers due to eddy/molecular 18 19 diffusion and returns a warning message if maximum values on any given day exceed 0.5 and the FTCS option is
- 20 selected.

BROM-transport also provides an option to divide the diffusion and sedimentation updates into smaller time steps related to the sources-minus-sinks time step by fixed factors, since the physical transport processes are often numerically limiting (Butenschön et al., 2012). The default time step is 0.0025 days or 216 seconds, which is much longer than the characteristic equilibration timescale of the CO_2 kinetics (Zeebe and Wolf-Gladrow, 2001).

26 2.2.3 BROM-transport vertical grid

27 The vertical grid in BROM-transport is divided into the pelagic water column, the BBL, and the sediments. The pelagic water column grid is either set as uniform with height/spacing set by the brom.yaml file (see Appendix 28 29 C), or it is read from the NetCDF forcing input file (see below), with an option to decrease resolution by 30 subsampling. In principle, the NetCDF input from the hydrodynamic model may already include a fully-resolved 31 BBL, but in practice we find this is rarely the case. BROM-transport therefore allows the user to "insert" a high-32 resolution BBL into the bottom of the input water column. This BBL has non-uniform grid spacing with layer 33 thickness decreasing geometrically towards the SWI, reaching O(cm) thickness for the fluff layer, based on 34 parameters from the brom.yaml file. For the upper sediments, the layer thickness is increased geometrically 35 moving down from the SWI, from O(mm) thickness in the surface layer to O(cm) thickness deeper in the 1 sediments, again based on brom.yaml parameters. The result is a full grid with non-uniform spacing and

- 2 maximum resolution near the SWI. As in many ocean models (e.g. ROMS, GOTM) the vertical grid in BROM-
- 3 transport is staggered: temperature, salinity, and biogeochemical concentrations are defined at layer midpoints,
- 4 while diffusivities, sinking/burial velocities, and resulting transport fluxes are all defined on layer interfaces.

5 2.2.4 BROM-transport initial conditions

6 Initial conditions for all concentrations in equations (1-3) can be provided by either using the initialization values 7 defined in the fabm.yaml file (see Appendix D) as uniform initial conditions for each variable, or by providing 8 the initial conditions for all variables at every depth in a text file with a specific format. Typically these initial 9 condition text files are generated by running the model to a steady state annual cycle and saving the final values 10 as the desired start date. Alternatively they could be generated by interpolating /smoothing data, in which case 11 the user should note that the input concentrations must be in units [mmol/m³ total volume].

12 2.2.5 BROM-transport boundary conditions

13 BROM-transport presently allows the user to choose between four different types of boundary conditions for 14 each variable and for upper and lower boundaries: 1) no-gradient at the bottom boundary (no diffusive flux) or 15 no-flux at the surface boundary, except where parameterized by the FABM biogeochemical model (i.e. for O₂ and DIC in the case of BROM-biogeochemistry); 2) a fixed constant value; 3) a fixed sinusoidal variation in 16 17 time defined by amplitude, mean value, and phase parameters; or 4) an arbitrary fixed variation in time read 18 from the input NetCDF file. All boundary condition options and parameters are set in the brom.yaml file (see 19 Appendix C). Note that options 2-4 are Dirichlet boundary conditions which define implicit fluxes of matter into 20 and out of the model domain, and that all boundary concentrations should be in units [mmol/m³ total volume 21 (water+solids)]. The default option 1 is generally the preferred choice, but the Dirichlet options can also be 22 useful to allow a simple representation of e.g. fluxes of nutrients into and out of the surface layer due to lateral 23 riverine input. A possible alternative is to use the forcings parameters for horizontal mixing (see equation (1)) to 24 specify horizontal exchanges or restoring terms to observed climatology (see section 2.2.7).

Under option 1, and using BROM-biogeochemistry, a surface O_2 flux representing exchange with the atmosphere is parameterized as:

27
$$Q_{o_2} = K_{660} * \left(\frac{Sc}{660}\right)^2 * (O_{2sat} - O_2)$$
 (12)

Where O_{2sat} is the oxygen saturation as a function of temperature and salinity, according to UNESCO (1986), Sc is the Schmidt number for oxygen (Raymond et al., 2012), and k_{660} is the reference gas-exchange transfer velocity, parameterized as $k_{660} = 0.365u^2 + 0.46u$ (Schneider et al., 2002) where u is the wind speed 10 m above the sea surface [m s⁻¹]. Air-sea exchange of CO₂ in BROM-biogeochemistry is parameterized using the partial pressures in water (pCO₂^{water}) and air (pCO₂^{air}) following the formulation and coefficients in (Butenschön

33 et al., 2016):

$$1 \qquad Q_{O_2} = F_{wind} * \left(pCO_2^{air} - pCO_2^{water} \right) \tag{13}$$

where $F_{wind} = (0.222u^2 + 0.333u)(Sc/660)^{-0.5}$ is a wind parameter (Nightingale et al., 2000), u is the wind speed, and Sc is the Schmidt number for CO₂ (Raymond et al., 2012).

4 2.2.6 BROM-transport irradiance model

BROM-transport includes two simple Beer-Lambert attenuation models to calculate in situ 24-hour average
photosynthetically active radiation (PAR) as needed by BROM-biogeochemistry and many other biogeochemical
models. The first is derived from the current ERSEM default model (Blackford et al., 2004; Butenschön et al.,
2016) and models the total attenuation as:

9
$$k_t = k_0 + k_{Phy}Phy + k_{PON}PON + k_s S$$
(14)

where k_0 is the background attenuation of seawater, k_{Phy} and k_{PON} are the specific attenuations due to phytoplankton and detritus respectively, and k_s is the specific attenuation due "other" optically active substances with concentration *S* (currently a constant input parameter). The second model includes attenuation due to other optically active concentrations that are modelled by BROM-biogeochemistry:

14
$$k_t = k_0 + k_{Phy}Phy + k_{PON}PON + k_{Het}Het + k_{DON}DON + k_{PB}B + k_{PIV}PIV + k_sS$$
(15)

where *B* is the total bacterial concentration (*Baae* + *Baan* + *Bhae* + *Bhan*) and *PIV* is the total volume fraction of modelled inorganic particles, calculated from the concentrations using input densities of each inorganic solid. The final irradiance is scaled by a constant parameter representing either the photosynthetically active fraction of the in situ irradiance or the relationship between surface PAR in water and the forcing surface irradiance (Mobley and Boss, 2012). The forcing surface irradiance *Eair(t)* can be read from NetCDF input or otherwise calculated using a sinusoidal function (Yakushev et al., 2013b). In addition, the surface attenuation due to ice cover can be accounted for as a simple linear function of a NetCDF input ice thickness variable *hice(t)*.

22 2.2.7 BROM-transport input forcings

BROM-transport requires forcing inputs at least for temperature, salinity, and vertical diffusivity at all depths in the pelagic water column and for each day of the simulation. These may be provided from an input subroutine that creates simple, hypothetical profiles, or from text/NetCDF files containing data from interpolations of measurements or hydrodynamic model output. Forcing time series of surface irradiance and ice thickness may also be read as NetCDF input. BROM-transport then uses these inputs in combination with parameters set in the run-time input file brom.yaml (see Appendix C) to solve the transport-reaction equations on a "full" vertical grid including pelagic water column, BBL, and sediment subgrids.

30 In order to run, BROM-transport must extend the input pelagic (temperature, salinity, diffusivity) forcings over

- 31 the full grid. Temperature and salinity in the BBL and sediments are set as uniform and equal to the values at the
- 32 bottom of the input pelagic water column for each day. The vertical diffusivity needs a more careful treatment

- 1 as it is the main defining characteristic of the pelagic vs. BBL vs. sediment environments. Within the water
- 2 column, the total vertical diffusivity $D = D_m + D_e$ for solutes and $D = D_e$ for particulates, where D_m is a constant
- 3 molecular diffusivity at infinite dilution, and D_e is the eddy diffusivity read from the input file for the pelagic
- 4 water column. For the BBL, D_e can be defined as "dynamic", in which case it is linearly interpolated for each
- 5 day between the deepest input forcing value above the SWI and zero at a depth h_{DBL} above the SWI, where h_{DBL}
- 6 is the diffusive boundary layer (DBL) thickness (default value 0.5 mm). This option is likely appropriate for
- shallow water applications where D_e may be strongly time-dependent within the user-defined BBL (default
- 8 thickness 0.5 m). Alternatively, a static, fixed profile $D_{eBBL}(z)$ may be more appropriate for deep-water BBLs,
- 9 where time dependence may be weak and deepest values from hydrodynamic models may be relatively far above
- 10 the SWI. In this case, BROM-transport offers two options for $D_{eBBL}(z)$: 1) a constant value, dropping to zero in
- 11 the DBL, or 2) a linear variation between a fixed value at the top of the BBL and zero at the top of the DBL.
- 12 Option 1) defines a simplest-possible assumption, while option 2) corresponds to the assumption of a log layer
- 13 for the current speed e.g. (Boudreau and Jorgensen, 2001; Holtappels and Lorke, 2011). Eddy diffusivity is
- strictly zero in the DBL, on the SWI, and within the sediments. Diffusivity in the sediments is due to molecular
- 15 diffusion and bioturbation and is parameterized as described in section 2.2.1.
- 16 Optional forcings for BROM-transport include 24-hour average surface irradiance Eair(t), which is often
- 17 supplied by hydrodynamic models (e.g. ROMS), a surface ice thickness forcing *hice(t)*, and depth-time arrays of
- horizontal mixing rates $\varepsilon_h(z,t)$ and horizontal mixing concentrations $\hat{C}_{0i}(z,t)$ (see equation (1)). Horizontal
- 19 mixing rates within the inserted BBL and sediments are set to zero. Note that these horizontal mixing forcings
- 20 can also be used to define relaxation or restoring fluxes to climatological values within the pelagic water column,
- which may in some cases provide a valid means of accounting for horizontal flux divergence effects that are missing in the 1D model.
- 23 **3 BROM demonstration run**

24 **3.1 Model setup**

A North Sea hydrodynamic scenario was used to demonstrate the ability of BROM to reproduce the biogeochemical mechanisms of oxic/anoxic transformations. Complete lists of the model options and parameter values used are given in Appendix C (brom.yaml input file for BROM-transport) and Appendix D (fabm.yaml input file for BROM-biogeochemistry).

29 The BROM-transport water column extended from 0 to 110 m, with a pelagic spatial resolution of 1 m inherited 30 from the GOTM hydrodynamic model used to provide forcings. A high-resolution BBL was inserted from 109.5 31 to 110 m, with layer thickness decreasing from approximately 25 cm to 3 cm in the fluff layer. Sediment grid 32 points were added to cover the upper 10 cm of sediments with layer thickness increasing from 0.5 mm in the 33 surface layer to 1 cm at depth. This choice of grid does not explicitly resolve the DBL (default thickness 0.5 34 mm) but the main DBL function of limiting solute exchange between the BBL and sediments is largely fulfilled 35 by the fluff layer (thickness 3 cm) and upper sediment layer (thickness 0.5 mm). The model time step for BROM-transport was set to 0.0025 days (216 seconds). 36

- 1 Upper boundary conditions included sinusoidal, time-varying Dirichlet boundary conditions for nitrate,
- 2 phosphate and silicate, implying net influxes and outfluxes of surface nutrients, as well as the default
- 3 parameterized air-sea fluxes of O_2 and DIC (see Appendix C). Lower boundary conditions assumed (by default)
- 4 zero diffusive flux for all reduced components (i.e. hydrogen sulfide, solid phase concentrations of metal sulfides
- 5 and carbonates, silicon and OM). The simulation therefore focuses on the consequences of the supply of fresh
- 6 OM as a main reducer in both water column and sediments.
- 7 The pelagic water column was forced by output from a GOTM hydrodynamical simulation for temperature,
- 8 salinity, and vertical diffusivity (taken from the salinity diffusivity) and surface irradiance calculated using the
- 9 sinusoidal option. We aimed for a solution representative for "present day" and therefore treated the GOTM
- 10 forcing as representative for a "normal year". BROM-transport was spun up from vertically-homogeneous initial
- 11 conditions for 100 model years with repeated-year forcings and boundary conditions. After this time, a quasi-
- 12 stationary solution with seasonally forced oscillations of the biogeochemical variables had been reached.
- 13 The results of these calculations were written to an output file in NetCDF format, including the daily vertical
- 14 distributions of model state variables, diagnostic rates of biogeochemical transformations, and fluxes associated
- 15 with diffusion and sedimentation. This output can be visualized by any NetCDF-compatible software.

16 **3.2 Results**

17 The model simulated the periodic replacement of oxic with anoxic conditions in the BBL following seasonal

- 18 mixing and OM production. The simulation demonstrates the characteristic features of biogeochemical profiles
- in the water column, BBL and upper sediments, as well as their variability under changing redox conditions(Figs. 2-4).
- 21 During intensive mixing conditions in winter, the water column is well oxygenated and the oxic/anoxic interface
- is located at several centimeters depth in the sediments (Figs. 2, 3). In summer, just after the spring bloom, an
- $23 \qquad \text{enrichment of the sediment surface with fresh OM and a restricted oxygen supply leads to the consumption of } O_2 \\$
- by OM mineralization and close to suboxic conditions (Fig. 2). The second bloom in autumn leads to a further
- 25 decrease of oxygen concentrations to complete depletion. There is a concomitant increase in reduced forms of
- (N, Mn, Fe) and finally of hydrogen sulfide in the bottom water (Figs. 2, 4). The redox interface thus moves
 from the sediment to the BBL.
- Figure 5 shows the rate of OM mineralization with a variety of electron acceptors. Oxygen is consumed during OM mineralization in summer and autumn and, after its complete depletion, denitrification dominates, with both nitrate reduction and nitrite reduction playing significant roles. The rate of mineralization of OM with Mn and Fe oxides is small, but as these processes prevent mineralization with sulfate, they cause a lag of a few days between the depletion of oxygen and the appearance of hydrogen sulfide in the water column (Figs. 2, 5). The amount of labile degradable OM is relatively small and mineralization with sulfate completely removes the
- 34 remaining OM, thus preventing methanogenesis (Fig. 5).
- 35 The seasonal variability of the sediment-water fluxes clearly demonstrates the appearance in the bottom water of
- 36 reduced forms of N, Mn, Fe and phosphate (Fig 6).

1 Generally, the concentrations, vertical distributions and benthic-pelagic fluxes of the parameters considered in

2 the model are reasonable and are within observed ranges for the North Sea (Queirós et al., 2014) and some other

3 regions with temporary bottom anoxia (Almroth et al., 2009; McCarthy et al., 2008; Morse and Eldridge, 2007;

- 4 Pakhomova et al., 2007; Queirós et al., 2014; Yu et al., 2015).
- 5

6 4 Conclusion and future work

7 This paper presents a description of BROM, a fully-coupled pelagic-benthic model that provides an integrated 8 framework to study the biogeochemistry of a water column and upper sediments. BROM simulates changes in 9 redox conditions and their impact on the distributions of a wide range of biogeochemical variables. In particular, 10 BROM provides a detailed description of the fate and availability of dissolved oxygen and hydrogen sulfide, the 11 former essential for macroscopic marine life, the latter highly toxic to it. BROM can therefore provide valuable 12 information to ecological studies, particularly in the context of multistressor impacts. The model suggests that 13 the timing of hydrogen sulfide release into the pelagic is linked to the dynamics of several electron acceptors that 14 are themselves of limited interest for biogeochemical and ecological purposes, and that are therefore rarely 15 included in models. The ability of BROM to simulate and forecast H₂S toxicity is in fact the direct result of its 16 inclusion of several of these rarely modelled chemical compounds (e.g., Mn(IV), Fe(III)). 17 This paper was not devoted to a detailed validation of BROM with in situ data; we plan to explore this in future 18 work. A qualitative analysis of the model results (Section 3) suggests that the model can produce realistic 19 distributions and fluxes of key biogeochemical variables during periodic changes in redox conditions. 20 In summary, we present a new benthic-pelagic biogeochemical model (BROM) that combines a relatively simple

21 pelagic ecosystem model with a detailed biogeochemical model of the coupled cycles of (N, P, Si, C, O, S, Mn,

22 Fe) in the water column, benthic boundary layer, and sediments, with a focus on oxygen and redox state. BROM

23 should be of interest for the study a range of environmental applications in addition to hypoxia, such as benthic

- 24 nutrient recycling, redox biogeochemistry, eutrophication, industrial pollution from trace elements, organic
- 25 loading, and ocean acidification
- 26

27 Code availability

28 The model as presented consists of two components. The first is a set of biogeochemical modules (brom/redox,

29 brom/bio, brom/carb, brom/eqconst), available as part of the official FABM distribution (<u>http://fabm.net</u>);

30 BROM-specific files are located in subdirectory src/models/niva/brom). The second is a hydrophysical driver

31 (BROM-transport) that provides the 1D vertical context and resolves transport; this is available separately from

32 <u>https://github.com/e-yakushev/brom-git.git</u>. When combined, the 1D BROM model as presented is obtained.

33 Both FABM and BROM-transport are coded in object-oriented Fortran 2003, have a build system based on

34 CMake (https://cmake.org), and use YAML files (http://yaml.org) for run-time configuration. The code is

- 1 platform independent and only requires a Fortran 2003-capable compiler, e.g., gfortran 4.7 or higher, or the Intel
- 2 Fortran compiler version 12.1 or higher. BROM-transport includes facilities for producing results as NetCDF
- 3 files, which can be read by a variety of software on different platforms.
- 4 Also you can run BROM without any Fortran compiler using a Win32 executable file which can be downloaded
- 5 from <u>https://github.com/e-yakushev/brom-git/releases/tag/v1.1</u>
- 6 As BROM's biogeochemical modules are built on FABM, they can be used from a wide range of 1D and 3D
- 7 hydrodynamic models, including GOTM, GETM, ROMS, MOM, NEMO and FVCOM (a ROMS-FABM
- 8 coupler has been developed by P.W.; NEMO-FABM and FVCOM-FABM couplers have been developed by the
- 9 Plymouth Marine Laboratory; contact J.B. for information).
- 10 Results shown in this paper were produced with BROM-transport tag v1.1. and the BROM-biogeochemistry
- 11 code in FABM tag v0.95.3, available from the above repositories. The simulation was run using the
- 12 netCDF/.yaml input files found in the data/ folder of the BROM-transport repository. However, we envisage
- 13 BROM to be further developed in a backward compatible manner, and encourage users to adopt the latest
- 14 version of the code. Step-by-step instructions for running BROM are found in Appendix A. Both FABM and
- 15 BROM-transport are distributed under the GNU General Public License (<u>http://www.gnu.org/licenses/</u>). As a
- 16 component of FABM, BROM-biogeochemistry is licensed under the same conditions as FABM.
- 17 Author contributions: Development of the model code was made by EY, EP, JB, PW, SY, analyses of the model results and
- 18 discussions were conducted by RB, RC and SP, and all authors contributed to the writing of the manuscript.
- 19

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32

33 Appendix A: Running BROM step-by-step

1. Installation. A Fortran-2003-capable compiler, e.g., gfortran 4.7 or higher, or the Intel Fortran compiler

35 version 12.1 or higher should be installed. In our demonstration we used the Intel Fortran Compiler version

36 15.0.4.221. Additionally, a NetCDF library compatible with the chosen Fortran compiler is required. CMake

- 37 software should be installed. After ensuring these prerequisites are in place, create a directory to hold the BROM
- 38 model code and associated input and output files. Detailed instructions for installation are provided at the BROM
- 39 repository https://github.com/e-yakushev/brom-git.git

- 1 2. <u>Preparation of input files.</u> The model reads two .yaml files with the model parameters (fabm.yaml and
- 2 brom.yaml), as well as a NetCDF or text file with the hydrophysical forcing data. Optionally the biogeochemical
- 3 initial conditions can be read from a text file **start.dat**; this may be a file written by a previous simulation (the
- 4 final model state is written to a file named **finish.dat** at the end of every simulation).
- 5 i. <u>brom.yaml</u> (see Appendix C). This file specifies the values of transport model parameters as well as various
- 6 option switches and input/output file and variable names. Text comments provide guidance and references for
- 7 setting parameter values. If using NetCDF input the user should pay careful attention to the NetCDF input
- 8 parameters and names, ensuring that this information is consistent with the input NetCDF file. The selected year
- 9 parameter year must refer to a year that is covered by the input forcing data.
- 10 ii. <u>fabm.yaml</u> (see Appendix D). This file specifies the values of biogeochemical model parameters , default
- 11 initial values for state variables, and the coupling of FABM modules. Text comments provide annotation and
- 12 references.
- 13 iii. <u>nns annual.nc</u> (in the example). This file contains input forcing data that may be derived from observations
- 14 or hydrodynamical model output (GOTM in our demonstration). It can be replaced by a text (.dat) file if this is
- 15 the format of the hydrodynamical model output.
- 16 iv. <u>start.dat</u>. Text file with initial values for model state variables at every depth. This file may be created by
- 17 renaming the output of a previous simulation (finish.dat: the state on 1st of January of the last modeled year).
- 18 3. <u>Output files</u>. These are NetCDF and headed text files generated automatically by the model during the
- simulation. Output files can be readily imported into various software packages for visualization and further
- 20 analysis. Certain output files (Vertical grid.dat and Hydrophysics.dat) are generated early in the simulation and
- should be checked by the user to ensure that the model grid and hydrophysical forcings are set up as intended.
- i. <u>Vertical_grid.dat.</u> Text file with model layer indices, midpoint depths, increments between midpoint depths,
 and thicknesses.
- ii. <u>Hydrophysics.dat</u>. Text file with daily profiles of hydrophysical variables (temperature, salinity, diffusivity, porosity, tortuosity, burial velocities).
- iii. <u>finish.dat</u>. Text file with the state variables for the 1st of January of the last modeled year. Can be used for
 visualization or as initial conditions for further calculations.
- iv. <u>output NNday.dat</u>. Optional text file with the state variables and diagnostic variables for day NN to make
 plots of vertical distributions (e.g. Fig. 3)
- v. <u>BROM_out.nc</u>. NetCDF file with daily profiles of state variables, rates of biogeochemical transformations,
 vertical fluxes.
- 32 4. <u>Visualization</u>. For NetCDF output files any software with NetCDF input can be used. In the example we used
- 33 PyNcView for 2D and BROM_pictures for 1D (available at
- 34 <u>https://github.com/BottomRedoxModel/brom_pictures</u>)
- 35

1 Appendix B: Derivation of burial velocities

2 The conservation equations for liquid and total solid volume fractions in the sediments can be written as:

$$3 \qquad \frac{\partial \varphi}{\partial t} = \frac{\partial}{\partial z} D_B^{inter} \frac{\partial \varphi}{\partial z} - \frac{\partial}{\partial z} u \varphi - \sum_{i=1}^{N_p} \rho_i^{-1} R_i \tag{B1}$$

$$4 \qquad \frac{\partial(1-\varphi)}{\partial t} = \frac{\partial}{\partial z} D_B^{inter} \frac{\partial(1-\varphi)}{\partial z} - \frac{\partial}{\partial z} w(1-\varphi) + \sum_{i=1}^{N_p} \rho_i^{-1} R_i$$
(B2)

5 where D_B^{inter} is the interphase bioturbation diffusivity (possibly non-zero only at the SWI), ρ_i is the density of the 6 i^{th} particulate substance, and R_i is the corresponding reaction term. Equations (B1) and (B2) assume that the 7 densities of liquid and total solid are both constant, and they retain the net contributions of reactive terms 8 although these are often considered negligible e.g. (Boudreau, 1997; Meysman et al., 2005). Summing (B1) and 9 (B2) and integrating over depth gives a useful and quite general relationship:

$$10 \quad \varphi u + (1 - \varphi)w = U \tag{B3}$$

where U(t) is only a function of time. If we now assume no externally impressed porewater flow, it follows that at some (possibly infinite) depth where compaction ceases $(\frac{\partial \varphi}{\partial z}=0, \varphi = \varphi_{\infty})$, the solute burial velocity *u* must here equal the particulate burial velocity *w*, hence $u_{\infty} = w_{\infty}$. Equation (B3) becomes:

$$14 \qquad \varphi u + (1 - \varphi)w = w_{\infty} \tag{B4}$$

Now assuming steady state compaction $(\frac{\partial \varphi}{\partial t}=0)$, equation (B2) can be integrated from the SWI to a depth *z* within the sediments:

17
$$(1-\varphi)w + D_B^{inter}\frac{\partial\varphi}{\partial z} = (1-\varphi_{SWI})w_{SWI} + D_{BSWI}^{inter}\frac{\partial\varphi}{\partial z_{SWI}} + \sum_i^{N_p}\frac{1}{\rho_i}\int_{z_{SWI}}^z R_i(z')dz'$$
(B5)

18 To determine the first term on the RHS of (B5), we assume that the total solid volume flux across the SWI is

19 equal to the total solid volume flux from the sinking of suspended particulate matter in the fluff layer:

20
$$(1 - \varphi_{SWI})w_{SWI} + D_{BSWI}^{inter} \frac{\partial \varphi}{\partial z_{SWI}} = F_b + \sum_i^{N_p} \frac{1}{\rho_i} v_{f(i)} \hat{C}_{sf(i)}$$
(B6)

21 where F_b defines a constant background solid volume flux due to non-modelled particles, $v_{f(i)}$ is the sinking

velocity in the fluff layer, and $\hat{C}_{sf(i)}$ is the suspended particulate concentration in the fluff layer. Substituting into (B5) we have:

24
$$(1-\varphi)w + D_B^{inter}\frac{\partial\varphi}{\partial z} = F_b + \sum_i^{N_p} \frac{1}{\rho_i} \Big[v_{f(i)} \hat{\mathcal{L}}_{sf(i)} + \int_{z_{SWI}}^z R_i(z') dz' \Big]$$
(B7)

25 Since $D_B^{inter} \frac{\partial \varphi}{\partial z}$ is zero at depth, the constant surface flux term is given by $F_b = (1 - \varphi_{\infty}) w_{b\infty}$, where both φ_{∞} 26 and $w_{b\infty}$ are input parameters. Hence we have:

27
$$(1-\varphi)w + D_B^{inter} \frac{\partial\varphi}{\partial z} = (1-\varphi_{\infty})w_{b\infty} + \sum_i^{N_p} \frac{1}{\rho_i} \Big[v_{f(i)} \hat{\mathcal{L}}_{sf(i)} + \int_{z_{SWI}}^{z} R_i(z') dz' \Big]$$
 (B8)

Equation (6) directly follows from (B8) by neglecting the modelled settling flux and reaction terms, then equation (7) follows by application of (B4). Equations (8) and (9) follow by considering the additional particulate burial velocity due to modelled fluxes and reactions (from the last term in B8) and applying (B4) to obtain the additional solute burial velocity.

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1 Table 1. State variables of BROM

Ν	Notation	Name	Units	Ν	Notation	Name	Units
	Ν	Nitrogen			0	Oxygen	
1	NH ₄	Ammonia	μΜ Ν	19	O ₂	Dissolved oxygen	μM O ₂
2	NO ₂	Nitrite	μΜ Ν		S	Sulfur	
3	NO ₃	Nitrate	μΜ Ν	20	H_2S	Hydrogen sulfide	μM S
4	PON	Particulate organic nitrogen	μΜ Ν	21	S ⁰	Total elemental sulfur	μM S
5	DON	Dissolved organic nitrogen	μΜ Ν	22	S_2O_3	Thiosulfate and sulfites	μM S
	Р	Phosphorus		23	SO_4	Sulfate	μM S
6	PO ₄	Phosphate	μΜ Ρ		С	Carbon	
	Si	Silicon		24	DIC	Dissolved inorganic carbon	μM C
7	Si	Dissolved silicon	μM Si	25	CH ₄	Methane	μM C
8	Si_part	Particulate silicon	μM Si	26	CaCO ₃	Calcium carbonate	μM Ca
	Mn	Manganese				Alkalinity	
9	Mn ²⁺	Dissolved bivalent manganese	μM Mn	27	Alk	Total alkalinity	μΜ
10	Mn ³⁺	Dissolved trivalent manganese	μM Mn				
11	Mn ⁴⁺	Particulate quadrivalent manganese	μM Mn			Ecosystem parameters	
12	MnS	Manganese sulfide	μM Mn	28	Phy	Phototrophic producers	μΜ Ν
13	MnCO ₃	Manganese carbonate	μM Mn	29	Het	Pelagic and benthic heterotrophs	μΜ Ν
	Fe	Iron		30	Bhae	Aerobic heterotrophic bacteria	μΜ Ν
14	Fe ²⁺	Dissolved bivalent iron	μM Fe	31	Baae	Aerobic autotrophic bacteria	μΜ Ν
15	Fe ³⁺	Particulate trivalent iron	μM Fe	32	Bhan	Anaerobic heterotrophic bacteria	μΜ Ν
16	FeS	Iron monosulfide	μM Fe	33	Baan	Anaerobic autotrophic bacteria	μΜ Ν
17	FeS ₂	Pyrite	μM Fe				
18	FeCO ₃	Ferrous Carbonate	μM Fe				

1 Table 2. Parameterization of the biogeochemical processes

2 2.1. Nutrients

Name of Process, reference, reaction	Parameterization in the model		
Nitrogen			
Autolysis (Savchuk and Wulff, 1996)	Autolysis = K_PON_DON* PON		
Mineralization at oxic conditions (Richards, 1965) $(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 106O_2 \rightarrow$ $106CO_2 + 16NH_3 + H_3PO_4 + 106H_2O$	DcDM_02 = K_DON_ox * DON * $\frac{0_2}{0_2 + \text{K}_0 \text{mox}_02}$ * (1 + beta_da $\frac{t^2}{t^2 + tda^2}$) DcPM_02 = K_PON_ox * PON * $\frac{0_2}{0_2 + \text{K}_0 \text{mox}_02}$ * (1 + beta_da $\frac{t^2}{t^2 + tda^2}$)		
Nitrification stage 1 (Canfield et al., 2005): $NH_4^++1.5O_2 \rightarrow NO_2^-+2H^+ + H_2O$	Nitrif1 = K_nitrif1 * NH_4 * O_2 * 0.5 * (1. +tanh($O_2 - O2s_nf$))		
Nitrification stage 2 (Canfield et al., 2005): $NO_2^- + 0.5 O_2 \rightarrow NO_3^-$	Nitrif2 = K_nitrif2 * NO_2 * O_2 * 0.5 * (1. +tanh($O_2 - O2s_nf$))		
Anammox (Canfield et al., 2005): $NO_2^- + NH_4^+ \rightarrow N_2 + 2H_2O$	Anammox = K_anammox * \mathbf{NO}_2 * \mathbf{NH}_4 * $(1 - 0.5 * (1 + \tanh(\mathbf{O}_2 - 02s_dn)))$		
POM denitrification 1st stage: (Anderson et al., 1982) $0.5CH_2O + NO_3^- \rightarrow NO_2^- + 0.5H_2O + 0.5CO_2$ 2d stage: (Anderson et al., 1982) $0.75CH_2O + H^+ + NO_2^- \rightarrow 0.5N_2 + 1.25H_2O + 0.75CO_2$	$Denitr1_PM = K_denitr1 * F_dnox * \frac{NO_3}{NO_3 + K_omno_no3} * PON$ $Denitr2_PM = K_denitr2 * F_dnox * \frac{NO_2}{NO_2 + K_omno_no2} * PON$ where $F_dnox = 1 - 0.5 * (1 + tanh(O_2 - O2s_dn))$ $DcPM_NOX = \frac{16}{212} * Denitr1_PM + \frac{16}{141.3} * Denitr2_PM$		

DOM denitrification (Anderson et al., 1982)	$Denitr1_DM = K_denitr1 * F_dnox * \frac{NO_3}{NO_3 + K_omno_no3} * DON$ $Denitr2_DM = K_denitr2 * F_dnox * \frac{NO_2}{NO_2 + K_omno_no2} * DON$ where F_dnox = 1 - 0.5 * (1 + tanh(O_2 - O2s_dn)) $DcDM_NOX = \frac{16}{212} * Denitr1_DM + \frac{16}{141.3} * Denitr2_DM$	
Phosphate		
Complexation with Mn(III) (Yakushev et al., 2007):	$mn_p_compl = (mn_ox2+mn_rd2-mn_ox1-mn_rd1)/r_mn_p$	
Complexation with Fe(III) (Yakushev et al., 2007):	fe_p_compl= (fe_rd-fe_ox1-fe_ox2+4.*DcDM_Fe+4.*DcPM_Fe)/r_fe_p	
Silicate		
Dissolution of particulate Si (Popova and Srokosz, 2009):	sipart_diss = Si_part * K_sipart_diss	
Complexation with Fe(III):	fe_si_compl= (fe_rd-fe_ox1-fe_ox2+4.*DcDM_Fe+4.*DcPM_Fe)/r_fe_si	

2.2. Redox metals and sulfur

Name of Process, reference, reaction	Parameterization in the model		
Manganese			
Manganese(II) oxidation (Canfield et al., 2005) $4Mn^{2+} + O_2 + 4H^+ \rightarrow 4Mn^{3+} + 2H_2O$	$mn_ox1 = 0.5 * (1 + tanh(Mn^{2+} - s_mnox_mn^2)) * K_mn_ox1 * Mn^{2+} * \frac{O_2}{(O_2 + K_mnox_o^2)}$		
Manganese (III) oxidation (Tebo et al., 1997) $2Mn^{3+}+3H_2O + 0.5O_2 \rightarrow 2MnO_2+6H^+$	mn_ox2 = 0.5 * (1 + tanh(Mn³⁺ - s_mnox_mn2)) * K_mn_ox2 * Mn³⁺ * $\frac{O_2}{(O_2 + K_mnox_o2)}$		
Manganese (IV) reduction (Canfield et al., 2005) $2MnO_2 + 7H^+ + HS^- \rightarrow 2Mn^{3+} + 4H_2O+S^0$	$mn_rd1 = 0.5 * \left(1 + tanh(\mathbf{Mn^{4+}} - s_mnrd_mn4)\right) * K_mn_rd1 * \mathbf{Mn^{4+}} * \frac{\mathbf{H_2S}}{(\mathbf{H_2S} + K_mnrd_hs)}$		
Manganese (III) reduction $2Mn^{3+} + HS^{-} \rightarrow 2Mn^{2+} + S^{0} + H^{+}$	$mn_rd2 = 0.5 * \left(1 + tanh(\mathbf{Mn^{3+}} - s_mnrd_mn3)\right) * K_mn_rd2 * \mathbf{Mn^{3+}} * \frac{\mathbf{H_2S}}{(\mathbf{H_2S} + K_mnrd_hs)}$		
MnS formation/dissollution (Davison, 1993) : Mn ²⁺ +HS ⁻ ↔MnS + H ⁺	mns_form = K_mns_form * max(0, $\left(\frac{\mathbf{H}_2 \mathbf{S} * \mathbf{M} \mathbf{n}^{2+}}{\mathbf{K}_m \text{nns} * \mathbf{H}^+} - 1\right)$) mns_diss = K_mns_diss * MnS * max(0, $\left(1 - \frac{\mathbf{H}_2 \mathbf{S} * \mathbf{M} \mathbf{n}^{2+}}{\mathbf{K}_m \text{nns} * \mathbf{H}^+}\right)$)		
MnCO ₃ precipitation/dissolution (Van Cappellen and Wang, 1996): Mn ²⁺ +CO ₃ ²⁻ ↔ MnCO ₃	mnco3_prec = K_mnco3_pres * max(0, $\left(\frac{\mathbf{Mn}^{2+} * \mathbf{CO}_3}{K_mnco3} - 1\right)$) mnco3_diss = K_mnco3_diss * $\mathbf{MnCO}_3 * \max(0, \left(1 - \frac{\mathbf{Mn}^{2+} * \mathbf{CO}_3}{K_mnco3}\right)$)		
MnCO ₃ oxidation by O ₂ (Morgan, 2000): $2 \text{ MnCO}_3 + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2 \text{ MnO}_2 + 2\text{HCO}_3^- + 2\text{H}^+$	$mnco3_ox = K_mnco3_ox * MnCO_3 * O_2$		
Manganese reduction for PON (Boudreau, 1996):	DcPM_Mn = K_PON_mn * PON * $\frac{Mn^{4+}}{Mn^{4+} + 0.5}$ * (1 - 0.5 * (1 + tanh($0_2 - 02s_dn$))		

$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 212MnO_2 + 318CO_2 + 106H_2O \rightarrow 424HCO_3^{-} + 212 Mn^{2+} + 16NH_3 + H_3PO_4$			
Manganese reduction for DON (Boudreau, 1996):	DcDM_Mn = K_DON_mn * DON * $\frac{Mn^{4+}}{Mn^{4+} + 0.5}$ * (1 - 0.5 * (1 + tanh(0 ₂ - 02s_dn))		
Iron			
Fe (II) oxidation with O ₂ (Van Cappellen and Wang, 1996): $4Fe^{2+} + O_2 + 10H_2O \rightarrow Fe(OH)_3 + 8H^+$	$fe_ox1 = 0.5 * (1 + tanh(Fe^{2+} - s_feox_fe^2)) * K_fe_ox1 * O_2 * Fe^{2+}$		
Fe (II) oxidation with Mn oxide (Van Cappellen and Wang, 1996): $2Fe^{2+} + MnO_2 + 4H_2O \rightarrow 2Fe(OH)_3 + Mn^{2+} + 2 H^+$	$fe_ox2 = 0.5 * (1 + tanh(Fe^{2+} - s_feox_fe^2)) * K_fe_ox2 * Mn^{4+} * Fe^{2+}$		
Fe (III) reduction (Volkov, 1984): $2Fe(OH)_3+HS^-+5H^+ \rightarrow 2Fe^{2+}+S^0+6H_2O$	$fe_rd = 0.5 * (1 + tanh(Fe^{3+} - s_feox_fe^{3})) * K_fe_rd * Fe^{3+} * \frac{H_2S}{H_2S + K_ferd_hs}$		
FeS formation/dissolition (Bektursunova and L'Heureux, 2011) : Fe ²⁺ + HS ⁻ ↔ FeS + H ⁺	$fes_prec = K_fes_form * max(0, \left(\frac{H_2S * Fe^{2+}}{K_fes * H^+} - 1\right))$ $fes_diss = K_fes_diss * FeS * max(0, \left(1 - \frac{H_2S * Fe^{2+}}{K_fes * H^+}\right))$		
FeS oxidation (Soetaert et al., 2007): FeS + 2.25O ₂ +2.5H ₂ O \rightarrow Fe (OH) ₃ + 2H ⁺ +SO ₄ ²⁻	$fes_ox = K_fes_ox * O_2 * FeS$		
Pyrite formation (Rickard and Luther, 1997; Soetaert et al., 2007): FeS+H ₂ S \rightarrow FeS ₂ +H ₂	$fes2_form = K_fes2_form * H_2S * FeS$		
Pyrite oxidation by O ₂ (Wijsman et al., 2002): $FeS_2+3.5O_2+H_2O \rightarrow Fe^{2+}+2SO_4^{2-}+2H^+$	$fes2_ox = K_fes2_ox * FeS_2 * O_2$		

FeCO ₃ precipitation/dissolution (Van Cappellen and Wang, 1996): Fe ²⁺ +CO ₃ ⁻ ↔ FeCO ₃	$feco3_form = K_feco3_form * max(0, \left(\frac{\mathbf{Fe}^{2+} * \mathbf{CO}_3}{K_feco3} - 1\right))$ $feco3_diss = K_feco3_diss * \mathbf{FeCO}_3 * max(0, \left(1 - \frac{\mathbf{Fe}^{2+} * \mathbf{CO}_3}{K_feco3}\right))$	
FeCO ₃ oxidation by O ₂ (Morgan, 2000): 2 FeCO ₃ + O ₂ + 2H ₂ O \rightarrow 2 FeO ₂ + 2HCO ₃ ⁻ + 2H ⁺	$feco3_ox = K_feco3_ox * FeCO_3 * O_2$	
Iron reduction for DON (Boudreau, 1996): $(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 424 Fe(OH)_3 + 742CO_2 \rightarrow$ $848HCO_3^{-} + 424 Fe^{2+} + 318 H_2O + 16NH_3 + H_3PO_4$	DcDM_Fe = K_DON_fe * DON * Fe ³⁺ * $(10.5 * (1 + tanh(O_2 - O2s_dn)))$	
Iron reduction for PON (Boudreau, 1996):	DcPM_Fe = K_PON_fe * PON * Fe ³⁺ * $(10.5 * (1 + tanh(O_2 - O2s_dn)))$	
Sulfur		
S ⁰ disproportionation (Canfield et al., 2005): $4S^0+3H_2O \rightarrow 2H_2S+S_2O_3^{2-}+2H^+$	$s0_disp = K_s0_disp * S^0$	
Sulphide oxidation with O ₂ (Volkov, 1984): $2H_2S + O_2 \rightarrow 2S^0 + 2H_2O$	$hs_ox = K_hs_ox * H_2S * O_2$	
S ⁰ oxidation with O ₂ (Volkov, 1984): $2S^0 + O_2 + H_2O \rightarrow S_2O_3^{2-} + 2H^+$	$s0_ox = K_s0_ox * S^0 * O_2$	
S ⁰ oxidation with NO ₃ (Kamyshny et al., 2013): $4S^0 + 3NO_3^- + 7H_2O \rightarrow 4SO_4^{2-} + 3NH_4^+ + 2H^+$	$s0_no3 = K_s0_no3 * NO_3 * S^0$	
$S_2O_3 \text{ oxidation with } O_2: (Volkov, 1984):$ $S_2O_3^{2-} + 2O_2 + 2OH^- \rightarrow 2SO_4^{2-} + H_2O$	$s2o3_ox = K_s2o3_ox * S_2O_3 * O_2$	
S ₂ O ₃ oxidation with NO ₃ : (Kamyshny et al., 2013)	$s2o3_no3 = K_s2o3_no3 * NO_3 * S_2O_3$	

$S_2O_3^{2-}+NO_3^{-}+2H_2O \rightarrow 2SO_4^{2-}+NH_4^{+}$	
Thiodenitrification: (Schippers and Jorgensen, 2002; Volkov, 1984) $5H_2S+8NO_3^-$ $+2OH^- \rightarrow 5SO_4^{2-} +4N_2 + 6H_2O$	$hs_no3 = K_hs_no3 * H_2S * NO_3$
POM sulfate reduction 1st and 2d stages (Boudreau, 1996): $(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 53SO_4^{2-} \rightarrow 106HCO_3^- + 16NH_3 + H_3PO_4 + 53H_2S$	$so4_rd_PM = K_so4_rd * F_sox * F_snx * SO_4 * PON$ $s2o3_rd_PM = K_s2o3_rd * F_sox * F_snx * S_2O_3 * PON$ $F_sox = 1 - 0.5 * (1. + tanh(O_2 - s_omso_o2))$ $F_snx = 1 - 0.5 * (1. + tanh(NO_3 - s_omso_no3))$ $DcPM_SO4 = \frac{16}{53} * (so4_rd_PM + s2o3_rd_PM)$
DOM sulfate reduction 1st and 2d stages (Boudreau, 1996):	$so4_rd_DM = K_so4_rd * F_sox * F_snx * SO_4 * DON$ $s2o3_rd_DM = K_s2o3_rd * F_sox * F_snx * S_2O_3 * DON$ $DcDM_SO4 = \frac{16}{53} * (so4_rd_PM + s2o3_rd_PM)$

2.3. Carbon and Alkalinity

Name of Process, reference, reaction	Parameterization in the model
CaCO ₃ formation/dissolution (Luff et al., 2001): Ca ²⁺ + CO ₃ ² \leftrightarrow CaCO ₃	$caco3_form = K_caco3_form * max(0, \left(\frac{Ca^{2+} * CO_3}{K_caco3} - 1\right))$ $caco3_diss = K_caco3_diss * CaCO_3 * max(0, \left(1 - \frac{Ca^{2+} * CO_3}{K_caco3}\right))^{4.5}$
CH ₄ formation from PON, methanogenesis (Boudreau, 1996) : (CH ₂ O) ₁₀₆ (NH ₃) ₁₆ H ₃ PO ₄ \rightarrow 53CO ₂ + 53CH ₄ + 16NH ₃ + H ₃ PO ₄	$\begin{aligned} & \text{DcPM}_{CH4} = \text{K}_{PON}_{ch4} * \text{F}_{sox} * \text{F}_{snx} * \text{F}_{ssx} * \text{CH}_{4} * \text{PON} \\ & \text{F}_{sox} = 1 - 0.5 * (1. + \tanh(\mathbf{O}_{2} - \text{s}_{o}\text{mso}_{o}2)) \\ & \text{F}_{snx} = 1 - 0.5 * (1. + \tanh(\mathbf{NO}_{3} - \text{s}_{o}\text{mso}_{n}03)) \\ & \text{F}_{ssx} = 1 - 0.5 * (1. + \tanh(\mathbf{SO}_{4} - \text{s}_{o}\text{mch}_{s}04)) \end{aligned}$
CH ₄ formation from DON, methanogenesis (Boudreau, 1996)	$DcDM_CH4 = K_DON_ch4 * F_sox * F_snx * F_ssx * CH_4 * DON$

CH ₄ oxidation by O ₂ (Boudreau, 1996) : CH ₄ + 2O ₂ + \rightarrow CO ₂ + 2H ₂ O	$ch4_o2 = K_ch4_o2 * CH_4 * O_2$
Alkalinity changes (Dickson, 1992; Wolf-Gladrow et al., 2007)	$ \begin{split} dAlk &= -\text{Nitrif1} + \text{Denitr2_PM} + \text{Denitr2_DM} + 2*(\text{so4}_{rd} + \text{s2o3}_{rd}) + \text{mn_ox1} - 3 \\ &* \text{mn_ox2} + 3* \text{mn_rd1} - \text{mn_rd2} - 2* \text{mns_form} + 2* \text{mns_diss} - 2 \\ &* \text{mnco3_form} + 2* \text{mnco3_diss} + 26.5*(\text{DcDM}_{Mn} + \text{DcPM}_{Mn}) - 2* \text{fe_ox1} \\ &- \text{fe_ox2} + 2* \text{fe_rd} - \text{fes_form} + \text{fes_diss} - 2* \text{fes_ox} - 2* \text{fes2_ox} + 53 \\ &* (\text{DcDM}_{Fe} + \text{DcPM}_{Fe}) - 0.5* \text{Disprop} + \text{s0_ox} - 0.5* \text{s0_no3} - \text{s2o3_ox} \\ &- 0.4* \text{hs_no3} - 2* \text{caco3_form} + 2* \text{caco3_diss} + \text{GrowthPhy}*\left(\frac{\text{LimN03}}{\text{LimN}}\right) \\ &- \text{GrowthPhy}*\left(\frac{\text{LimNH4}}{\text{LimN}}\right) \end{split} $

2.4. Ecosystem processes

Name of Process, reference, reaction	Parameterization in the model	
Phytoplankton		
Influence of the irradiance on photosynthesis	$LimLight = (\frac{Iz}{Iopt}) * e^{(1-Iz/Iopt)}$	
Influence of temperature on photosynthesis	$\text{LimT} = e^{(\text{bm}*t-\text{cm})}$	
Dependence of photosynthesis on P	$\operatorname{LimP} = \frac{(\mathbf{P0}_4/\mathbf{Phy})^2}{(\mathrm{K_po4_lim*r_n_p})^2 + (\mathbf{P0}_4/\mathbf{Phy})^2}$	
Dependence of photosynthesis on NO ₃	$\text{LimNO}_{3} = \frac{((\text{NO}_{3} + \text{NO}_{2})/\text{Phy})^{2}}{K_{\text{nox}}\text{lim}^{2} + ((\text{NO}_{3} + \text{NO}_{2})/\text{Phy})^{2}} \exp(-K_{\text{mox}} \sin \frac{(\text{NH}_{4}/\text{Phy})^{2}}{K_{\text{mh}}^{4} - (\text{NH}_{4}/\text{Phy})^{2}})$	
Dependence of photosynthesis on NH ₄	$\operatorname{LimNH}_{4} = \frac{\left(\frac{\mathrm{NH}_{4}}{\mathrm{Phy}}\right)^{2}}{K_{nh4}\operatorname{lim}^{2} + \left(\frac{\mathrm{NH}_{4}}{\mathrm{Phy}}\right)^{2}} (1 - \exp(-K_{psi}\frac{(\mathrm{NH}_{4}/\mathrm{Phy})^{2}}{K_{nh4}\operatorname{lim}^{2} + (\mathrm{NH}_{4}/\mathrm{Phy})^{2}}))$	
Influence of N on photosynthesis	$LimN = LimNO_3 + LimNH_4$	
Growth of phytoplankton	GrowthPhy = K_phy_gro * LimLight * LimT * min (LimP, LimN) * Phy	
Excretion rate of phytoplankton	ExcrPhy = K_phy_exc * Phy	
Phytoplankton mortality rate	$MortPhy = (K_phy_mrt + 0.45 * (0.5 - 0.5 * tanh(0_2 - 60)) + 0.45 * (0.5 - 0.5 * tanh(0_2 - 20))) * Phy$	
Heterotrophs		
Grazing of Heterotrophs	Grazing = GrazPhy + GrazPOP + GrazBact	
Grazing of Het. on phytoplankton	GrazPhy = K_het_phy_gro * Het * $\frac{(Phy/(Het + 10^{-4}))^2}{K_het_phy_lim^2 + (Phy/(Het + 10^{-4}))^2}$	

Grazing of Het. on detritus	$GrazPOP = K_het_pom_gro * Het * \frac{(\frac{PON}{Het + 10^{-4}})^2}{K_het_pom_lim^2 + (\frac{PON}{Het + 10^{-4}})^2}$	
Grazing of Het. on bacteria	GrazBact = GrazBaae + GrazBaan + GrazBhae + GrazBhan	
Grazing of Het. on bacteria autotrophic aerobic	GrazBaae = K_het_pom_gro * Het * $\frac{(Baae/(Het + 10^{-4}))^2}{\lim GrazBac^2 + (Baae/(Het + 10^{-4}))^2}$	
Grazing of Het. on bacteria autotrophic anaerobic	GrazBaan = 0.5 * K_het_pom_gro * Het * $\frac{(\text{Baan}/(\text{Het} + 10^{-4}))^2}{\text{limGrazBac}^2 + (\text{Baan}/(\text{Het} + 10^{-4}))^2}$	
Grazing of Het. on bacteria heterotrophic aerobic	GrazBhae = K_het_pom_gro * Het * $\frac{(Bhae/(Het + 10^{-4}))^2}{\lim GrazBac^2 + (Bhae/(Het + 10^{-4})^2)}$	
Grazing of Het. on bacteria heterotrophic anaerobic	GrazBhan = $1.3 * K_het_pom_gro * Het * \frac{(Bhan/Het + 0.0001)^2}{\lim GrazBac^2 + (Bhan/Het + 10^{-4})^2}$	
Respiration rate of Het.	RespHet = K_het_res * Het * $(0.5 + 0.5 * tanh(0_2 - 20))$	
Mortality of Het.	MortHet = Het * $\begin{pmatrix} 0.25 + 0.3 * (0.5 - 0.5 * \tanh(0_2 - 20)) \\ + 0.45 * (0.5 + 0.4 * \tanh(\mathbf{H}_2\mathbf{S} - 10)) \end{pmatrix}$	
Bacteria		
Growth rate of Bacteria aerobic autotrophic	$(ChemBaae = Nitrif1 + Nitrif2 + mn_ox1 + fe_ox1 + s2o3_ox + s0_ox + anammox) * k_{Baae_{gro}} * Baae * min(\frac{(NH_4 / ((Baae + 10^{-4})^2)}{limBaae^2 + (NH_4 / (Baae + 10^{-4}))^2}, \frac{(PO_4 / (Baae + 10^{-4}))^2}{limBaae^2 + (PO_4 / (Baae + 10^{-4}))^2})$	
Rate of mortality of Bacteria aerobic autotrophic	$MortBaae = K_Baae_mrt + K_Baae_mrt_h2s * 0.5 * (1 - tanh(1 - H_2S)) * Baae^2$	

Growth rate of Bacteria aerobic heterotrophic	$HetBhae = (DcPM_02 + DcDM_02) * K_Bhae_gro * Bhae * \frac{(DON/(Bhae+10^{-4}))^2}{limBhae^2 + (DON/(Bhae+10^{-4}))^2}$
Rate of mortality of Bacteria aerobic heterotrophic	$MortBhae = K_Bhae_mrt + K_Bhae_mrt_h2s * Bhae * 0.5 * (1 - tanh(1 - H_2S))$
Growth rate of Bacteria anaerobic autotrophic	ChemBaan = $(mn_rd1 + mn_rd2 + fe_rd + hs_ox + hs_no3) * K_Baan_gro * Baan$ $* \min(\frac{(NH4/(Baan + 10^{-4}))^2}{\lim Baan^2 + (NH4/(Baan + 10^{-4}))^2}$
Rate of mortality of Bacteria anaerobic autotrophic	MortBaan = K_Baan_mrt * Baan
Growth rate of Bacteria anaerobic heterotrophic	$HetBhan = (DcPM_NOX + DcDM_NOX + DcDM_Mn + DcPM_Mn + DcDM_Fe + DcPM_Fe + DcDM_SO4 + DcPMSO4 + DcDM_CH4 + DcPM_CH4) * K_Bhan_gro * Bhan* \frac{(DON/(Bhan + 10^{-4}))^2}{\lim Bhan^2 + (DON/(Bhan + 10^{-4}))^2}$
Rate of mortality of Bacteria anaerobic heterotrophic	$MortBhan = K_Bhan_mrt + K_Bhan_mrt_o2 * Bhan * (0.5 + 0.5 * tanh(1 - O_2))$
Summarized OM mineralization	Dc_OM_total = DcDM_O2 + DcPM_O2 + DcPM_NOX + DcDM_NOX + DcDM_Mn + DcPM_Mn + DcDM_Fe + DcPM_Fe + DcDM_SO4 + DcPM_SO4 + 0.5 * (DcDM_CH4 + DcPM_CH4)

 Table 3. Parameters names, notations, values and units of the coefficients used in the model

Table 3.1. Nutrients and oxygen

Parameter	Notation	Units	Value	Reference ranges
Nitrogen				
Specific rate of DON oxidation of with O ₂	K_DON_ox	d-1	1*10-2	0.1 (Savchuk, 2002)
Specific rate of PON oxidation of with O ₂	K_PON_ox	d-1	2*10-3	0.002 (Savchuk, 2002)
Temperature control threshold coefficient for OM decay	Tda	°C	13	13 (Burchard et al., 2006)
Temperature control coefficient for OM decay	beta_da	-	20	20 (Burchard et al., 2006)
Half-saturation constant of O ₂ for OM mineralization	K_omox_o2	μΜ	1	1 (Yakushev, 2013)
Specific rate of autolysis, PON to DON	K_PON_DON	d-1	0.1	0.02 (Burchard et al., 2006)
Half saturation constant for uptake of NO ₃ +NO ₂	K_nox_lim	μΜ	0.12	0.5 (Gregoire and Lacroix, 2001)
Half saturation constant for uptake of NH ₄	K_nh4_lim	μΜ	2*10-2	0.2 (Gregoire and Lacroix, 2001)
Strength of NH4 inhibition of NO3 uptake constant	K_psi	-	1.46	1.46 (Gregoire and Lacroix, 2001)
Specific rate of the 1st stage of nitrification	K_nitrif1	d ⁻¹	1*10-2	0.01 (Yakushev, 2013)
Specific rate of the 2d stage of nitrification	K_nitrif2	d-1	0.1	0.1 (Yakushev, 2013)
Specific rate of 1st stage of denitrification	K_denitr1	d-1	0.16	0.16 (Yakushev and Neretin, 1997), 0.5 (Savchuk, 2002)
Specific rate of 2d stage of denitrification	K_denitr2	d-1	0.25	0.22 (Yakushev, Neretin, 1997)
Half-saturation of NO ₃ for OM denitrification	k_omno_no3	μM N	1*10-3	1*10 ⁻³ (Yakushev, 2013)
Half-saturation of NO ₂ for OM denitrification	k_omno_no2	μM N	1*10-3	1*10 ⁻³ (Yakushev, 2013)
Specific rate of thiodenitrification	K_hs_no3	$\mu M^{-1} d^{-1}$	0.8	0.8 (Yakushev and Neretin, 1997), 0.015 (Gregoire and Lacroix, 2001)
Specific rate of anammox	K_anammox	d-1	0.8	0.8 (Gregoire and Lacroix, 2001), 0.03 (Yakushev et al., 2007)
	Oxygen	-	•	
Half-saturation constant for nitrification	O2s_nf	μΜ	5.	10 (Gregoire and Lacroix, 2001)
Half-saturation constant for denitrification anammox, Mn reduction	O2s_dn	μΜ	10	40 (Savchuk, 2002)
Threshold value of O ₂ for OM mineralization	s_omox_o2	μМ	1*10-2	1*10 ⁻² (Yakushev, 2013)
Threshold value of O ₂ for OM denitrification	s_omno_o2	μΜ	25	25 (Yakushev, 2013)
Threshold value of O ₂ for OM sulfate reduction	s_omso_o2	μM	25	25 (Yakushev, 2013)
Threshold value of NO for OM sulfate reduction	s_omso_no3	μΜ	5	5 (Yakushev, 2013)

Stoichiometric coefficients				
N/P	r_n_p	-	16	(Richards, 1965)
O/N	r_o_n	-	6.625	(Richards, 1965)
C/N	r_c_n	-	8	(Richards, 1965)
Si/N	r_si_n	-	1	(Richards, 1965)
Fe/N	r_fe_n	-	26.5	(Boudreau, 1996)
Mn/N	r_mn_n	-	13.25	(Boudreau, 1996)
Phosph				
Half-saturation constant for uptake of PO ₄ by phytoplankton	K_po4_lim	μΜ	0.02	0.01 (Yakushev et al., 2007)
Fe/P ratio in complexes with Fe oxides	r_fe_p		2.7	(Yakushev et al., 2007)
Mn/P ratio in complexes with Mn(III)	r_mn_p		0.67	(Yakushev et al., 2007)
Silicon				
Specific rate of Si dissolution	K_sipart_diss	d-1	0.008	0.008 (Popova, Srokosz, 2009)
Half-saturation constant for uptake of Si by phytoplankton	K_si_lim	-	0.1	0.1 (Popova and Srokosz, 2009)
Fe/P ratio in complexes with Fe oxides	r_fe_si		2.7	2.7 (Yakushev et al., 2007)

Table 3.2. Redox metals and sulfur

Parameter	Notation	Units	Value	Reference ranges
Manganese				
Specific rate of Mn(II) oxidation to Mn(III) with O ₂	K_mn_ox1	d-1	0.1	0.18-1.9 M/yr; (Tebo, 1991) 2 d ⁻¹ ; (Yakushev et al., 2007)
Specific rate of Mn(IV) reduction to Mn(III) with H ₂ S	K_mn_rd1	d-1	0.5	22 d ⁻¹ ; (Yakushev et al., 2007)
Specific rate of Mn(III) oxidation to Mn(IV) with O ₂	K_mn_ox2	d-1	0.2	18 d ⁻¹ ; (Yakushev et al., 2008)
Specific rate of Mn(III) reduction to Mn(II) with H ₂ S	K_mn_rd2	d-1	1	0.96-3.6 M/yr; (Tebo, 1991) 2 d ⁻¹ ; (Yakushev et al., 2007)
Specific rate of formation of MnS from Mn(II) and H ₂ S	K_mns_form	d-1	1*10-5	Assumed
Specific rate of dissolution of MnS to Mn(II) and H ₂ S	K_mns_diss	d-1	5*10-4	Assumed
Solubility product for MnS	K_mns	М	1500	7.4*10 ⁻¹⁸ M (Brezonik and Arnold, 2011)
Solubility product for MnCO ₃	K_mnco3	М	1	3.4*10 ⁻¹⁰ -10 ⁻¹³ M(Jensen et al., 2002)

Specific rate of MnCO ₃ formation	K_mnco3_form	d ⁻¹	3*10-4	$10^{-4} - 10^{-2}$ mol/g yr; (Wersin, 1990); (Wollast, 1990)
Specific rate of MnCO ₃ dissolution	K_mnco3_diss	d-1	7*10-4	$10^{-2} - 10^3$ yr ⁻¹ ; (Wersin, 1990; Wollast, 1990)
Specific rate of MnCO3 oxidation	K_mnco3_ox	d-1	27*10-4	Assumed
Specific rate of DON Oxidation with Mn(IV)	K_DON_Mn	d-1	1*10-3	1*10 ⁻³ (Yakushev et al., 2007)
Specific rate of PON Oxidation with Mn(IV)	K_PON_Mn	d-1	1*10-3	1*10 ⁻³ (Yakushev et al., 2007)
Threshold value of Mn(II) oxidation	s_mnox_mn2	μM Mn	1*10-2	1*10 ⁻² (Yakushev et al., 2007)
Threshold value of Mn(III) oxidation	s_mnox_mn3	μM Mn	1*10-2	1*10 ⁻² (Yakushev et al., 2007)
Threshold value of Mn(IV) reduction	s_mnrd_mn4	μM Mn	1*10-2	1*10 ⁻² (Yakushev et al., 2007)
Threshold value of Mn(III) reduction	s_mnrd_mn3	μM Mn	1*10-2	1*10 ⁻² (Yakushev et al., 2007)
Half saturation constant of Mn oxidation	K_mnox_o2	$\mu M O_2$	2	2 (Yakushev et al., 2007)
Iron			•	
Specific rate of Fe(II) to Fe(III) oxidation with O ₂	K_fe_ox1	d-1	0.5	2*10 ⁹ M/yr; (Boudreau, 1996); 4 d ⁻¹ ; (Yakushev et al., 2007)
Specific rate of Fe(II) to Fe(III) oxidation with MnO ₂	K_fe_ox2	d-1	1*10-3	10 ⁴ -10 ⁸ M/yr; (Boudreau, 1996); 1 d ⁻¹ ; (Yakushev et al., 2007)
Specific rate of Fe(III) to Fe(II) reduction with H ₂ S	K_fe_rd	d-1	0.5	1*10 ⁴ M/yr;(Boudreau, 1996); 0.05d ⁻¹ ; (Yakushev et al., 2007)
Solubility product for FeS	K_fes	μΜ	2510	2.51*10 ⁻⁶ mol/cm ³ (Bektursunova and L'Heureux, 2011)
Specific rate of FeS formation from Fe(II) and H ₂ S	K_fes_form	d-1	5*10-4	5*10 ⁻⁶ -10 ⁻³ M/yr; (Boudreau, 1996; Hunter et al., 1998); (Bektursunova and L'Heureux, 2011)
Specific rate of FeS dissolution to Fe(II) and H ₂ S	K_fes_diss	d-1	1*10 ⁻⁶	1*10 ⁻³ yr ⁻¹ (Hunter et al., 1998); (Bektursunova and L'Heureux, 2011)
Specific rate of FeS oxidation with O ₂	K_fes_ox	d-1	1*10-3	2*10 ⁷ –3*10 ⁵ M/yr; (Boudreau, 1996); (Van Cappellen and Wang, 1996)
Specific rate of DON oxidation with Fe(III)	K_DON_fe	d ⁻¹	5*10-5	5*10 ⁻⁵ (Yakushev et al., 2007)
Specific rate of PON oxidation with Fe(III)	K_PON_fe	d-1	1*10-5	1*10 ⁻⁵ (Yakushev et al., 2007)
Specific rate of FeS ₂ formation by reaction of FeS with H ₂ S	K_fes2_form	d ⁻¹	1*10-6	8.9*10 ⁻⁶ M/day; (Rickard and Luther, 1997)

Specific rate of FeS ₂ oxidation with O ₂	K_fes2_ox	d-1	4.4*10-4	(Bektursunova and L'Heureux, 2011)
Threshold value of Fe(II) reduction	s_feox_fe2	μM Fe	1*10-3	1*10 ⁻³ (Yakushev et al., 2007)
Threshold value of Fe(III) reduction	s_ferd_fe3	μM Fe	1*10-2	1*10 ⁻² (Yakushev et al., 2007)
Solubility product for FeCO ₃	K_feco3	μМ	15	3.8*10 ⁻¹¹ -6.4*10 ⁻¹² M (Jensen et al., 2002)
Specific rate of FeCO ₃ dissolution	K_feco3_diss	d ⁻¹	7*10-4	2.5*10 ⁻¹ -10 ⁻² yr ⁻¹ ; (Wersin, 1990; Wollast, 1990)
Specific rate of FeCO ₃ formation	K_feco3_form	d-1	3.4*10-4	10 ⁻⁶ –10 ⁻² mol/g yr; (Boudreau, 1996; Wersin, 1990; Wollast, 1990)
Specific rate of FeCO ₃ oxidation with O ₂	K_feco3_ox	d-1	2.7*10-3	Assumed
Sulfur				
Specific rate of H_2S oxidation to S^0 of with O_2	K_hs_ox	d-1	0.5	0.5 (Yakushev et al., 2007)
Specific rate of S^0 oxidation of with O_2	K_s0_ox	d-1	2*10-2	2*10 ⁻² (Yakushev et al., 2007)
Specific rate of S ⁰ oxidation of with NO ₃	K_s0_no3	d-1	0.9	0.9 (Yakushev et al., 2007)
Specific rate of S_2O_3 oxidation with O_2	K_s2o3_ox	d-1	1*10-2	1*10 ⁻² (Yakushev et al., 2007)
Specific rate of S ₂ O ₃ oxidation with NO ₃	K_s2o3_no3	d-1	1*10-2	1*10 ⁻² (Yakushev et al., 2007)
Specific rate of OM reduction with sulfate	K_so4_rd	d-1	5*10-6	5*10 ⁻⁶ (Yakushev et al., 2007)
Specific rate of OM reduction with thiosulfate	K_s2o3_rd	d-1	1*10-3	1*10 ⁻³ (Yakushev et al., 2007)
Specific rate of S ⁰ disproportionation	K_s0_disp	d-1	1*10-3	1*10 ⁻³ (Yakushev et al., 2007)
Half-saturation of Mn reduction	K_mnrd_hs	μM S	1	1 (Yakushev et al., 2007)
Half-saturation of Fe reduction	K_ferd_hs	μM S	1	1 (Yakushev et al., 2007)

Table 3.3. Carbon

Parameter	Notation	Units	Value	Reference ranges
Specific rate of CaCO ₃ dissolution	K_caco3_diss	d-1	3	wide ranges are given in (Luff et al., 2001)
Specific rate of CaCO ₃ formation	K_caco3_prec	d-1	2*10-4	wide ranges are given in (Luff et al., 2001)
Solubility product constant for CaCO3	K_caco3			Calculated as a function of T, S (Roy et al., 1993)
Specific rate of CH ₄ formation from DON	K_DON_ch4	d-1	5*10-5	(Lopes et al., 2011)

Specific rate of CH ₄ formation from PON	K_PON_ch4	d-1	1*10 ⁻⁵	(Lopes et al., 2011)
Specific rate of CH ₄ oxidation with O ₂	K_ch4_o2	$uM^{-1}d^{-1}$	0.14	0.14 (Lopes et al., 2011)
Specific rate of CH ₄ oxidation with SO ₄	K_ch4_so4	uM ⁻¹ d ⁻¹	0.000027 4	(0.0274 m3 /mol-1 day-1 (Lopes et al., 2011)

Table 3.4. Ecosystem parameters

Parameter	Notation	Units	Value	Reference ranges
Bacteria	I			
Baae maximum specific growth rate	K_Baae_gro	d-1	2*10-2	2*10 ⁻² (Yakushev et al., 2007)
Baae specific rate of mortality	K_Baae_mrt	d-1	5*10 ⁻³	5*10 ⁻³ (Yakushev et al., 2007)
Baae increased specific rate of mortality due to H ₂ S	K_Baae_mrt_h2s	d-1	0.899	0.899 (Yakushev et al., 2007)
Bhae maximum specific growth rate	K_Bhae_gro	d ⁻¹	0.5	0.5 (Yakushev et al., 2007)
Bhae specific rate of mortality	K_Bhae_mrt	d-1	2*10-2	2*10 ⁻² (Yakushev et al., 2007)
Bhae increased specific rate of mortality due to H ₂ S	K_Bhae_mrt_h2s	d-1	0.799	0.799 (Yakushev et al., 2007)
Baan maximum specific growth rate	K_Baan_gro	d-1	0.12	0.12 (Yakushev et al., 2007)
Baan specific rate of mortality	K_Baan_mrt	d-1	1.2*10-2	1.2*10 ⁻² (Yakushev et al., 2007)
Bhan maximum specific growth rate	K_Bhan_gro	d ⁻¹	0.19	0.19 (Yakushev et al., 2007)
Bhan specific rate of mortality	K_Bhan_mrt	d-1	7*10 ⁻³	7*10 ⁻³ (Yakushev et al., 2007)
Bhan increased specific rate of mortality due to O ₂	K_Bhan_mrt_o2	d ⁻¹	0.899	0.899 (Yakushev et al., 2007)
Limiting parameter for bacteria grazing by Het	limGrazBac	-	2	2 (Yakushev et al., 2007)
Limiting parameter for bacteria anaerobic heterotrophic	limBhan	-	2	2 (Yakushev et al., 2007)
Limiting parameter for bacteria aerobic heterotrophic	limBhae	-	5	5 (Yakushev et al., 2007)
Limiting parameter for bacteria anaerobic autotrophic	limBaan	-	2	2 (Yakushev et al., 2007)
Limiting parameter for nutrient consumption by Baae	limBaae	-	2	2 (Yakushev et al., 2007)
Phytoplankto)n			
Maximum specific growth rate	K_phy_gro	d-1	4.8	0.9-1.3 (Savchuk, 2002), 3.0 (Gregoire and Lacroix, 2001)
Optimal irradiance	Iopt	W m ⁻²	25	50 (Savchuk, 2002)
1 st coefficient for growth dependence on t	bm	°C-1	0.12	0.12 (Burchard et al., 2006)
2 ^d coefficient for growth dependence on t	cm	-	1.4	1.4 (Burchard et al., 2006)

Specific rate of mortality	K_phy_mrt	d ⁻¹	0.15	0.3-0.6 (Savchuk, 2002), 0.05 (Gregoire and Lacroix, 2001)
Specific rate of excretion	K_phy_exc	d-1	0.05	0.01 (Burchard et al., 2006)
Heterotrophs	•	-		•
Maximum specific rate of grazing of Het on Phy	K_het_phy_gro	d-1	1.0	0.9 (Gregoire and Lacroix, 2001), 1.5 (Burchard et al., 2006)
Half-saturation constant for the grazing of Het on Phy for Phy/Het ratio	K_het_phy_lim	-	1.1	1 (Yakushev et al., 2007)
Maximum specific rate of grazing of Het on POM	K_het_pom_gro	d-1	0.7	1.2 (Burchard et al., 2006)
Specific respiration rate	K_het_res	d-1	0.02	1 (Yakushev et al., 2007)
Half-saturation constant for the grazing of Het on POM in dependence to ratio POM/Het	K_het_pom_lim	-	0.2	0.2 (Yakushev et al., 2007)
Maximum specific rate of mortality of Het	K_het_mrt	d-1	0.05	0.05(Gregoire and Lacroix, 2001)
Food absorbency for Heterotrophs	Uz	-	0.5	0.5-0.7 (Savchuk, 2002)
Ratio between dissolved and particulate excretes of Heterotrophs	Hz	-	0.5	0.5 (Gregoire and Lacroix, 2001)

Table. 3.5. Sinking

Parameter	Notation	Units	Value	Reference ranges
Rate of sinking of Phy	Vphy	m d ⁻¹	1	0.1-0.5 (Savchuk, 2002)
Rate of sinking of Het	Vhet	m d ⁻¹	1	1 (Yakushev et al., 2007)
Rate of sinking of bacteria (Bhae, Baae, Bhan, Baan)	Vbact	m d ⁻¹	0.4	0.5 (Yakushev et al., 2007)
Rate of sinking of detritus (PON)	Vsed	m d ⁻¹	6	0.4 (Savchuk, 2002), 1-370 (Alldredge and Gotschalk, 1988)
Rate of sinking of inorganic particles (Fe and Mn hydroxides, carbonates)	Vm	m d ⁻¹	8	6-18 (Yakushev et al., 2007)

Table 4. Rates of biogeochemical production/consumption of the model compartments

Table 4.1. Nutrients and oxygen

Parameter	Rate
O ₂	$ \begin{array}{l} R \ O_2 = (GrowthPhy - RespHet - \ DcDM_02 - \ DcPM_02) * r_o_n - 0.25 * mn_ox1 - 0.25 * mn_ox2 - 0.25 * fe_ox1 - 0.5 * ns_ox - 0.5 * s0_ox - 0.5 * s2o_3ox - 0.5 * mns_ox - 1.5 * Nitrif1 - 0.5 * Nitrif2 - 2.25 * fes_ox - 3.5 * fes_ox - 0.5 * mnco3_ox + feco_3_ox - 2 * ch4_o2 \end{array} $
Particulate Organic Nitrogen (PON)	R PON = MortBaae + MortBaan + MortBhae + MortBhan + MortPhy + MortHet + Grazing * (1 – Uz) * (1 – Hz) – GrazPOP) – autolysis – DcPM_O2 – DcPM_NOX – DcPM_SO4 – DcPM_Mn – DcPM_Fe – 0.5 * DcPM_CH4
Dissolved Organic Nitrogen (DON)	R DON = autolysis – DcDM_O2 – DcDM_NOX – DcDM_SO4 – DcDM_Mn – DcDM_Fe – 0.5 * DcPM_CH4 – HetBhae – HetBhan + ExcrPhy + Grazing * (1 – Uz) * Hz
NH4	$R NH_4 = Dc_OM_total - Nitrif1 - anammox + 0.75 * s0_ox + s2o3_ox - ChemBaae - ChemBaan + RespHet - GrowthPhy * \frac{LimNH4}{LimN}$
NO ₂	$R \text{ NO}_2 = \text{ Nitrif1} - \text{ Nitrif2} + \text{ Denitr1} - \text{ Denitr2} - \text{ anammox} - \text{ GrowthPhy} * \frac{\text{LimN03}}{\text{LimN}} * \frac{\text{NO}_2}{\text{NO}_2 + \text{NO}_3 + 10^{-5}}$
NO ₃	$R NO_{3} = Nitrif2 - Denitr1 - 1.6 * hs_no3 - 0.75 s0_ox - s2o3_ox - GrowthPhy * \left(\frac{LimNO_{3}}{LimN}\right) * * \left(\frac{NO_{3} + 10^{-5}}{NO_{2} + NO_{3} + 10^{-5}}\right)$
PO ₄	$R PO_{4} = \frac{GrowthPhy + RespHet + Dc_OM_total - ChemBaae - ChemBaan}{r_n_p} + fe_p_compl + mn_p_compl$
Si	R Si= (ExcrPhy-GrowthPhy)*r_si_n +fe_si_compl
Si particulate	$R Si part = -K_sipart_diss * Si part + (MortPhy + GrazPhy) * r_si_n)$

Table 4.2. Redox metals and sulfur

Parameter	Rate
Mn(II)	R Mn2 = mn_rd2 - mn_ox1 + mns_diss - mns_form - mnco3_form + mnco3_diss + 0.5 * fe_ox2 + (DcDM_Mn + DcPM_Mn) * r_mn_n
Mn(III)	$R Mn3 = mn_ox1 - mn_ox2 + mn_rd1 - mn_rd2$
Mn(IV)	$RMn4 = mn_ox2 - mn_rd1 - 0.5 * fe_ox2 + mnco3_ox - (DcDM_Mn + DcPM_Mn) * r_mn_n$

MnS	R MnS = mns_form - mns_diss
MnCO ₃	R MnCO ₃ = mnco3_form - mnco3_diss - mnco3_ox
Fe(II)	$R Fe2 = fe_rd - fes_form - fe_ox1 - fe_ox2 + fes_diss - feco3_form + feco3_diss + fes2_ox + 4 * r_fe_n * (DcDM_Fe + DcPM_Fe)$
Fe(III)	$R Fe3 = fe_ox1 + fe_ox2 - fe_rd + fes_ox + feco3_ox - 4 * r_fe_n * (DcDM_Fe + DcPM_Fe)$
FeS	$R FeS = fes_form - fes_diss - fes_ox - fes2_form$
FeS ₂	$R FeS_2 = fes2_form - fes2_ox$
FeCO ₃	$R FeCO_3 = feco3_form - feco3_diss - feco3_ox$
H_2S	$ \label{eq:rescaled} \begin{array}{l} R \ H_2 S \ = \ 0.5 * s0_disp \ -hs_no3 + s2o3_rd \ -fes2_form \ -0.5 * mn_rd1 \ -0.5 * mn_rd2 \ -0.5 * fe_rd \ -hs_ox \ +fes_diss \ -fes_form \ +mns_diss \ -mns_form \end{array} $
S ⁰	$R S^{0} = hs_ox + 0.5 * mn_rd1 + 0.5 * mn_rd2 + 0.5 * fe_rd - s0_ox - s0_disp - s0_no3$
S ₂ O ₃	$R S_2 O_3 = 0.5 * s0_o x - s2o3_o x + 0.25 * s0_d isp + 0.5 * so4_r d - 0.5 * s2o3_r d - s2o3_n o$
SO ₄	$R SO_4 = hs_no3 - so4_rd + 0.5 * s2o3_ox + s0_no3 + 2 * s2o3_no3 + fes_ox + 2 * fes2_ox$

Table 4.3. Carbon and alkalinity

Parameter	Rate
DIC	R DIC = caco3_diss - caco3_form - mnco3_form + mnco3_diss + mnco3_ox - feco3_form + feco3_diss + feco3_ox + (Dc_OM_total - ChemBaae - ChemBaan - GrowthPhy + RespHet) * r_c_n
CaCO3	$R CaCO3 = caco3_form - caco3_diss$
CH4	$R CH4 = ch4_form - ch4_ox$
Total alkalinity	R Alk = dAlk

 Table 4.4. Ecosystem parameters

Parameter Rate	Parameter	Rate
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Phytoplankton	R Phy = GrowthPhy – MortPhy – ExcrPhy – GrazPhy
Heterotrophs	R Het = Uz * Grazing – MortHet – RespHet
Aerobic heterotrophic bact.	R Bhae = HetBhae – MortBhae – GrazBhae
Aerobic autotrophic bact.	R Baae = ChemBaae – MortBaae – GrazBaae
Anaerobic heterotrophic bact.	R Bhan = HetBhan – MortBhan – GrazBhan
Anaerobic autotrophic bact.	R Baan = ChemBaan – MortBaan – GrazBaan

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Figure 1. Flow-chart of biogeochemical processes represented in the Benthic RedOx Model (BROM), showing the transformation of sulphur species (a), the ecological block (b), the transformation of nitrogen species (c), the transformation of iron species (d), the processes affecting dissolved oxygen (e), the carbonate system and alkalinity (f), and the transformation of manganese species (g).



Figure 2. Simulated seasonal variability of the selected modelled chemical parameters (µM), in the water column (top panels) and in the benthic boundary layer and sediments (bottom panels).



Figure 3. Vertical distributions of the modelled chemical parameters (μ M), biological parameters (μ M N), temperature ($^{\circ}$ C), salinity (PSU) and vertical diffusivity ($10^{-3}m^2s^{-1}$) during the winter period of well-mixed conditions, showing the water column (light blue), the benthic boundary layer (dark blue), and the sediments (light brown).



Figure 3 contd. Vertical distributions of the modelled chemical parameters (µM) and biological parameters (µM N) during the winter period of well-mixed conditions, showing the water column (light blue), the benthic boundary layer (dark blue), and the sediments (light brown).



Figure 4. Vertical distributions of the modelled chemical parameters (μ M), biological parameters (μ M N), temperature (°C), salinity (PSU) and vertical diffusivity (10⁻³m²s⁻¹) during the period of bottom anoxia, showing the water column (light blue), the benthic boundary layer (dark blue), and the sediments (light brown).



Figure 4 contd. Vertical distributions of the modelled chemical parameters (μ M) and biological parameters (μ M N) during the period of bottom anoxia, showing the water column (light blue), the benthic boundary layer (dark blue), and the sediments (light brown).



Figure 5. Simulated seasonal variability of biogeochemical transformation rates just above the sediment water interface, showing the rates of DON mineralization with oxygen, nitrate, nitrite, Mn(IV), Fe(III), SO4, S2O3, and CH4 production from DON. Units are mmol m⁻³ d⁻¹.



Figure 6. Simulated seasonal variability of vertical diffusive fluxes from the benthic boundary layer to the sediments of oxygen, hydrogen sulphide, nitrate, silicate, ammonia, Mn(II) and Fe(II). Positive fluxes are downward and negative fluxes are upward. Units are mmol $m^{-2} d^{-1}$.