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**Modelling macro nutrients in shelf sea sediments: fitting model output to experimental data using a genetic algorithm**

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**Abstract**

*Purpose:* Diagenetic modelling, the mathematical simulation of the breakdown of sedimentary organic matter and subsequent fate of associated nutrients, has progressed to a point where complex, non-steady-state environments can be accurately modelled. A genetic algorithm has never been used in conjunction with an early-diagenetic model, and so we aim to discover whether this method is viable to determining a set of realistic model parameters, which itself is often a difficult task.

*Materials and methods:* A range of sensitivity analyses were conducted to establish the parameters for which the model was most sensitive before a micro genetic algorithm was used to fit output from a previously published diagenetic model (OMEXDIA) to observational data, taken at the North Dogger Site from a series of cruises in the North Sea. Profiles of carbon, oxygen, nitrate and ammonia were considered. The method allows a set of parameters to be determined in a manner analogous to natural selection. Each iteration of the genetic algorithm within each experiment decreases the variance between the observed profiles and those calculated by OMEXDIA.

*Results and discussion:* Despite some of the observed profiles, particularly for carbon, showing unusual patterns, the genetic algorithm was able to generate a set of parameters which was able to fit the observations. The genetic algorithm can therefore help to determine the values of other parameters used in the model, for which observational values are difficult to measure (e.g. the flux of organic matter to the sediment from the overlying water column and the rates of degradation of organic matter). We also show that the values of the parameters determined by the micro genetic algorithm technique are able to be used in a potentially temporally predictive manner.

*Conclusions:* The micro genetic algorithm used is a viable method to fit carbon and nutrient sedimentary profiles observed in complex, dynamic shelf sea systems, despite OMEXDIA originally being designed for a different sedimentary environment. The results therefore show that this novel use of a genetic algorithm is a suitable method for both model calibration and validation, and that the technique may help in explaining processes which are poorly understood.

**Keywords** Diagenetic modelling • Early-diagenesis • Genetic algorithm • North Sea • Parameter optimisation • Sedimentary biogeochemistry

**1 Introduction**

Early diagenesis, the bacteria-mediated degradation of organic matter in aquatic sediments, is an important process in the wider biogeochemical cycling of nutrients important to life, such as carbon, oxygen, and nitrogen, and is particularly important in shelf seas. In brief, early diagenesis refers to the set of reactions leading to the breakdown of organic matter; the order of these reactions is controlled by the thermodynamics and kinetics of the reactions, with more energetically-favourable reactions happening first, tending to be closer to the sediment-water interface (Froelich et al. 1979; Burdige 2006). The reactions associated with early diagenesis, including secondary reactions such as the reoxidation of reduced compounds, and the order they occur in, are well defined (Froelich et al. 1979). The dominant reactions in coastal waters and shelf seas with oxic bottom-waters, such as the North Sea, are oxic mineralisation of organic matter, denitrification and sulphate reduction (van Raaphorst et al. 1990; Henrichs 1992; Upton et al. 1993; Bottrell et al. 2009). Shelf seas are particularly important in global nutrient cycling, as they cover approximately 8% of the global ocean surface area and have been estimated to account for 80% of organic matter burial and 90% of sedimentary mineralisation (Wollast 1991), making them one of the most biogeochemically active areas of the biosphere (Gattuso et al. 1998).

Models of diagenesis have been developed to simulate porewater nutrient profiles and fluxes, both in order to increase our understanding of the systems and to develop a predictive ability so that certain features of future sedimentary environments and distribution of compounds can be calculated (e.g. Van Cappellen and Wang 1996; Boudreau 1996; Canfield et al. 1996; Dhakar and Burdige 1996; Berg et al. 2003; Soetaert et al. 1996b). One important step in model development is to match model output to experimental data. Previous work has shown how models can replicate experimental results (Soetaert et al. 1996b), and genetic algorithms are common in most branches of ecosystem and biogeochemical modelling (e.g. Ward et al. 2010); however, they have had little application in diagenetic modelling, with only one other group having carried out work in this area to date (Wilson, 2011). Here we show how a genetic algorithm can be used to enhance a general modelling approach by fitting model output to observational data. Where these parameters mirror observations taken in the field it can also be used as a method for estimating values for these observations, which can be particularly helpful when observational data is difficult to obtain.

**2 Methods**

 The experimental data have been gathered from the North Sea as part of the Marine Ecosystems Connections Program (Cefas 2011). Over the course of two years (2007 and 2008), a series of cruises were carried out allowing physical, biological and chemical data to be collected at three sites (North Dogger, Oyster Grounds and Sean Gas Fields) at four different times of year (pre-Spring Bloom, post-Spring Bloom, post-Summer bloom / autumn and Winter); Full site details and some preliminary results can be found in Greenwoodet al. (2010), but of particular importance are the measurements of oxygen, nitrate, and ammonia that have been used here .

 The model we have used for this work is OMEXDIA; although a full description of OMEXDIA is given in Soetart *et al*. (1996b), a brief explanation of the model will be given here. OMEXDIA was developed to simulate sedimentary cycling of key chemical species involved in early diagenesis, and so carbon, oxygen, nitrate and ammonia are explicitly included (Froelich et al. 1979). The reduced form of all other electron acceptors involved in early diagenesis (i.e. Mn2+, S2-, Fe2+), as well as methane, which is produced as a result of methanogenesis, are lumped together in a single variable known as the Oxygen Demand Unit; the name of this parameter reflects the ability of all reduced species to be reoxidised by oxygen. The model uses Michaelis-Menten equations to enable limitation and inhibition of each diagenetic reaction (i.e. oxic mineralisation is limited only by the concentration of oxygen, whereas denitrification is inhibited by the concentration and limited by the concentration of nitrate). The forcing parameter of the model is the flux of organic matter to the sediment from the overlying water column; three separate organic carbon fractions are included: fast, slow and refractory (although in practice, only fast and slow are modelled, while any carbon which is not mineralised is deemed to be refractory); separate mineralisation rate constants and nitrogen:carbon ratios can be applied to each fraction. Porosity is included in the model to accurately calculate the proportion of solid matter which is organic carbon and the porewater concentrations of the oxidants. The model domain is 15 cm, divided into 100 layers, and porosity decreases exponentially thoughout the domain, from 0.9 to 0.7; solid phase constituents are affected by bioturbation throughout the mixed layer depth (i.e. the depth of the sediment throughout which bioturbation is deemed to occur, initially set at 5 cm). Diffusion coefficients are applied to each of the solute species, while, additionally, ammonia has an adsorption coefficient, allowing adsorption onto solid particles to be a sink term for ammonia.

 The version of the model described in Soetaert et al. (1996b), including the parameter set given there, will now be referred to as the default model. For the present work, we have used the steady-state version of the model.

 A full sensitivity analysis was carried out on the model to gain information on which parameters the model was most sensitive to, using three different approaches. During each approach, each parameter was changed individually and the steady-state solution of the model was found. The results were then compared with the output from a default model run, using the parameter values given in Soetaert *et al.* (1996b), by way of a cost function as shown in Equation 1.

 Equation 1

where *i* is the chemical species being considered (O2, or NH3), *e*1 is concentration in the current layer (from 1 to 100) in the standard run and *e*2 is the concentration in the current layer in the sensitivity analysis experiment.

 Three approaches were used, with each consisting of two model runs (a low parameter value, and a high parameter value) for each of the 26 parameters. This resulted in a total of six separate experiments consisting of a total of 156 model runs in order to use to draw conclusions about the sensitivity of each parameter. Three approaches were used rather than one to give a wide range of conditions to test the model’s sensitivity, given its complexity and non-linearity. The three approaches taken were as follows: to double (for the high value) and halve (for the lower value) the default parameters; to increase and decrease the default parameters by an order of magnitude, and to use selected values obtained after a comprehensive literature search. The default values for each parameter and the literature values used are shown in Table 1. The values chosen from the literature were picked to be representative of the environments that we are trying to model, i.e. shallow shelf seas, whereas OMEXDIA was originally calibrated to represent continental slope sediment. It was therefore expected that the literature values we use may be very different to the ones presented in Soetaert *et al.* (1996b). Each parameter was scored after each of the six experiments, and the parameters were ranked after all six experiments had been conducted; the results for this experiment are shown in Table 1, and indicate that carbon flux to the sea floor and the oxygen content of the overlying water column were the two most important parameters. The parameters to which the model was most sensitive to were used to try and fit model output to experimental data by eye, by varying the value of these parameters. It was quickly established that this was an inefficient and time-consuming method to attempt to fit the model to experimental data. This led to the genetic algorithm approach being used. The ranked parameters from the sensitivity analysis allowed the genetic algorithm to be applied, to discover if there was a sensible set of parameters which could both describe the experimental data and be used subsequently in a predictive manner.

 The genetic algorithm approach used was a micro genetic algorithm (μGA), which is a technique comparable to natural selection. The method used was the same as described in detail by Ward *et al*. (2010), and the basics are given here. The μGA is allowed to pick a random value within a set range for each of the unconstrained parameters; the parameter vector that this generates is known as a ‘species’. The ranges are given to the algorithm in advance, and are selected to be representative of values which are deemed sensible from the literature. The model was run numerous times (*n*), each time with a different random parameter set where typically *n* is chosen to match the number of model parameters (26); this set of *n* runs is collectively known as a generation. In the experiments described here, we not only fit the model parameters but also the main model forcing parameter (carbon flux to the sediment). After each generation, the difference between each species and the observations is calculated; the species with the smallest *misfit* value (i.e. closest to the data) is passed unchanged to the next generation. The misfit (*M*) is calculated according to Equation 2, and shows that the misfit is calculated in a sum of least squares method, with the standard error of the sums of the differences between the observational data points (*cj* ) and the modelled values (*cmod*) at each layer depth (*i*) being summed to give an integrated misfit value for the entire sediment column for each chemical species (*s*: carbon, oxygen, nitrate and ammonia). The integrated misfit values for each of the four chemical species were then also summed to give a final misfit value for each of the species in the generation.

|  |  |
| --- | --- |
|  | Equation 2 |

 In Equation 2, *i* is the layer depth, *j* is the current repeat measurement at depth *i*, and SE is the standard error of the observational data at depth *i*. SE was used to remove bias that would otherwise be introduced as a result of the different units in the observations of the four different chemical species.

 Weighted genetic crossover is also applied to the parameter vectors, to generate the rest of the next generation. Probability, weighted according to the size of their misfit, is used to combine two species. Combination is analogous to genetic crossover, such that a single random point is picked along the parameter vectors, and all the values past this point are swapped between the two species. The number of generations, chosen at the start of the run, was set at 5000. Each genetic algorithm experiment was repeated ten times with no changes in the range of each parameter (below, this is called a set of experiments); it was decided that this would give the optimal compromise between computational time and the chance of finding a reasonable fit; despite the large parameter space used, the number of runs would not be too computationally intensive but would still give a good assessment of the μGA approach.

 In the experiments described here, we attempted to fit the model to the porewater observations of oxygen, nitrate and ammonia made at the North Dogger site in the North Sea (see Greenwood et al. 2010 for full site details), using all available data, including repeat measurements on each cruise. The experimental procedure used for the μGA was as follows: initially, the five most sensitive parameters were used, and allowed to vary by double and half of the default OMEXDIA parameters; the exception to this being when experimental values were available, where the observed range was used instead. As the default parameters were based on continental slope data, which are likely to give different values in all model parameters to shelf-sea values, it was decided to additionally allow the constrained parameters some freedom, and these parameters were given a range of 10% above and below the value used in the base model. We recognise that some of the model parameters will increase in value between the intended (continental slope) use and the current (shelf) use, whereas other parameters will decrease. A 10% variance was picked to signify that the two environments are very different, and the results from the sensitivity analysis and attempts at manual fitting indicated that it would be extremely difficult and computationally expensive to fit the data when only a small number of parameters were allowed to vary. The results from this set of experiments was then visually analysed. For each set of experiments where the magnitude and shape of the calculated profiles did not correlate with the observational data, the number of free parameters was increased by three (each set of three being the three next most sensitive parameters) before rerunning the μGA. During this iterative process, increased ranges were given to those parameters where the μGA calculated a value for that parameter which was one of the two boundary values of the given range for that parameter; the range was increased by allowing the value of the boundary value to halve if the lower boundary value was calculated, and increase by 50% if the upper boundary value was calculated. This approach of attempting to use a limited number of parameters was initially chosen to limit the computational effort required; however, it became clear that profiles that were representative of the observational data were not being generated when a limited number of parameters were used.

 A final experiment (experiment 2) was therefore carried out where all 26 parameters were allowed greater freedom – the given range was up to two orders of magnitude for some parameters. Table 1 contains full details of the parameter values used in this run.

**3 Results**

Following the sensitivity analysis experiments, the values for each parameter were ranked for each of the three approaches; for each parameter, the ranks from the individual runs were summed to give an overall score, from which all the parameters could be ranked. The resulting ranked list is shown in Table 1. In general, the parameters that the model is most sensitive to are those for which the most is known biogeochemically, and which are known to have significant effects in natural systems. For example, the most sensitive parameter is the flux of carbon to the sediment. As this is the forcing parameter (*i*.*e*. the parameter which drives the kinetics and biogeochemistry of the rest of the system), it would be expected that the model should be particularly sensitive to it. The next five most sensitive parameters were overlying O2 concentration, nitrogen:carbon ratio in fast degrading organic matter, overlying NH3 concentration, bioturbation coefficient and rate of nitrification, which are all parameters for which observational data is available.

 Throughout this section, the modelled profiles will be described with reference to the observed profiles. We have used the calculated misfit value to determine the goodness of fit, but this also correlates with visual similarity with regard to the shape and magnitude of features in the profiles. The values of M appear large, even for the modelled profiles which appear visually very similar to the observed profiles. This, however, is only an artefact of the method used due to the large number of repeat measurements and that 100 depth intervals were used. The value of the misfit calculated for the experiment which generated Figure 1 (3077.8) were the smallest seen throughout all experiments, and were 10 orders of magnitude smaller than the largest misfits calculated in this experiment. In the majority of the first 100 generations of this experiment, the modelled profiles of the four species did not visually match the shape of the observed profiles, leading to the very large misfit values.

Fig. 1 shows the result from one μGA run (from experiment 2) where the resulting profiles match the observational data relatively well. As can be seen in Fig. 1, the algorithm is mainly able to accurately represent the relatively unusual carbon profile, where the carbon concentrations do not decrease steadily throughout the sediment as might be expected due to the degradation of OM by the various electron acceptors, and instead decreases from a mean of 0.57% to 0.43% in the top 10 mm before remaining relatively constant. The algorithm is not, however, able to resolve the very fast degradation of the OM in the top 10 mm, with the TOC values decreasing from a maximum of 0.45% in the uppermost layer to a mean value of 0.42% below 10 mm. This is the same mean value as the observations in the sediment below 10 mm. The oxygen profile, which shows the oxygen penetration depth (OPD) as being approximately 12 mm, is correctly represented, as is the single ammonia profile used in this μGA run. Fig. 1 also shows the algorithm’s ability to correctly generate both the concentration magnitude (12.9 mmol m-3) and depth (8 mm) of the nitrate peak (which is caused by nitrification in the oxic zone, above the denitrification boundary, and therefore falls within the oxic zone), before the decrease in concentration of nitrate due to its use as an electron acceptor, although there appears to be two outliers in the nitrate peak. We should also state that if the experiments showed that 5000 generations was an excess of the number actually required (data not shown). In all cases, the misfit fell to within 1% of the final value within 100 generations.

 A second µGA experiment was carried out, using only North Dogger site data from the 2007 cruises. This additionally allowed us to validate the model using North Dogger 2008 data. For this μGA run, the same parameter ranges were used as in the first μGA experiment. The fit from the 2007 data can be seen in Fig. 2, showing, as would be expected, a relatively good fit; as when using the whole data set, the model does not resolve the very fast decay of OM in the top 10 mm. The model also appears to slightly over-estimate the OPD by approximately 3 mm, although this is likely to be affected by the oxygen profile in February 2007, which is likely to be caused by a worm-hole, significantly increasing the oxygen concentrations that would otherwise be expected. The nitrate peak also seems to be slightly over estimated (the model peak concentration is 9.6 mmol m-3, in comparison with a maximum observed value of 6.68 mmol m-3), although without much higher resolution in vertical profile measurements, this would be difficult to verify. The ammonia profile shows the expected increase in concentration as OM is oxidised, before the concentration stabilises, implying that this is below the depth at which all labile OM has been oxidised. The modelled mean ammonia concentration in this zone is 49.2 mmol m-3, compared to an observed mean value of 51.6 mmol m-3.

 Fig. 3 shows model output using the parameter set obtained from this µGA run against 2008 data (no TOC data is yet available from the 2008 cruises) which provides an initial validation for OMEXDIA using shelf-sea data; experimental data from the 2008 cruises have been used for those parameters where we have data (bottom water concentrations of oxygen, nitrate and ammonia); as no carbon data is yet available from 2008, the N:C ratios have continued to be set as the 0.086 and 0.16 in the slow and fast degrading organic matter respectively.

 The model slightly overestimates oxygen concentrations for the 2008 data, and also overestimates the OPD by approximately 5 mm. Although the model estimates the concentration (9.6 mmol m-3 compared to the observed value of 10.5 mmol m-3) and depth (10 mm) of the nitrate peak well, it slightly underestimates the nitrate concentration in the sediment below this point. Nitrate concentrations never reaching zero in the observations implies that there is sufficient nitrate to oxidise all available labile OM; this is also reflected in the ammonia concentrations, which stabilise at approximately the same depth (75 mm) as nitrate concentrations. The ammonia model profile matches the observations well, with the ammonia concentrations stabilising approximately only 3 mm below the observations. The modelled ammonia concentration in this zone is 50.9 mmol m-3, compared to an observed value of 39.8 mmol m-3.

**4 Discussion**

 Although the results shown in this paper indicate that OMEXDIA can be fitted to observations from different environments for which it was intended, this was only achieved at a relatively large computational expense for a 1-dimensional model. Each single μGA took approximately 25 hours to complete, and more than 50 runs were completed; however, due to the large number of parameters, the wide range of parameter space used, and the fitting algorithm employed by a μGA (Ward et al. 2010), there is still unspecified uncertainty as to whether the set of parameters shown here are the best possible fit.

 Although there are recognised uncertainties in the methods and limitations in the data, the μGA used here has come very close to recreating the profiles shown by the experimental data despite OMEXDIA originally being designed to fit profiles found in continental margin areas (Soetaert et al. 1996b; Soetaert et al. 1996a). As a result of the random seeding of the genetic algorithm, there is uncertainty as to how frequently profiles which are deemed to fit well will be generated. In the experiments carried out for this paper, one run in the final set provided profiles which had a much lower misfit value (and hence were visually much closer) than any of the other 9 runs in that set, although it is not possible to say if good profiles will always be generated in 10% of cases. In the remaining 9 parameter sets generated, at least one of the profiles was extremely inaccurate, either in shape or magnitude of the features; these inaccuracies were reflected in large misfit values. It should also be recognised that no fitting algorithm can ever guarantee an optimal solution, due to the methods implemented, nor is it possible to calculate a set of parameter values that would generate a misfit value of zero. There may also be uncertainties related to the observational data, and how this affects the parameter set generated by the algorithm, although we have attempted to overcome this by using the total range of all available observational data.

 The observational data used here do not show stereotypical profiles for early diagenesis. For example, the largely uniform carbon profiles from the 2007 data do not show a decrease of carbon with depth, as would normally be expected. This is most likely to be attributed to the importance of the benthic fluff layer; benthic fluff was observed above the sediment-water interface (SWI) during these cruises (pers. comm. E.R. Parker); there is also a wide spread of data at all depths in the sediment column, possibly attributable to the high productivity in both the water column and sediment leading to a relatively large density of macrozoobenthos in these sediments (Baptist et al. 2006). The observed TOC profiles imply that the benthic fluff contains the vast majority of fast degrading organic matter (although it is important to bear in mind that, although OMEXDIA contains three carbon fractions, the reality is that the TOC is composed of large number of carbon compounds degradable over a wide spectrum of time scales). The TOC profiles do show a sharp decrease in the top 2 mm, particularly in February, from a value of 0.75% to a value of 0.45%. By 6 mm, the mean value of TOC is 0.48%, falling to 0.41% at 150 mm. The relatively high values in the top 2 mm are due to high concentrations of labile organic matter in the oxic zone close to the SWI, before being oxidised by oxygen and nitrate. The values of TOC observed between 6 and 150 mm are in line with other observations from similar areas of the North Sea (e.g. Upton et al. 1993; van Raaphorst et al. 1990; van Raaphorst and Malschaert 1996; Boon and Duineveld 1998; de Haas et al. 1997). It is therefore likely that the majority of fast degradable OM is mineralised in the water column, leading to only slow degrading OM being mineralised in the sediment. The observed profiles of O2, NO3¯and NH3 agree with this interpretation of the TOC profile. The oxic water column is able to mineralise all of the fast degradable TOC that is in the benthic fluff layer, and also leads to an oxic sediment. The oxygen in the sediment is rapidly consumed, by mineralisation of OM, by oxidation of ammonia to nitrate, leading to the nitrate peak which coincides with the oxic-suboxic boundary, and by the reoxidation of other electron acceptors. NO3¯ is reduced to NH3 below this boundary, leading to the slight decrease in TOC as already described, and also leading to the increase of NH3 as shown in Fig. 3.

 The observed profiles do also show specific patterns. Oxygen in particular shows very strong seasonal trends; as a result of the spring bloom, O2 concentrations at the SWI drop from 200 mmol m-3 in February 2007 to ~90 mmol m-3 in April 2007, recovering to pre-spring bloom values by September. However, by a sediment depth of 10 mm, there is little spread in the concentrations of O2. Perhaps rather surprisingly, there is little seasonal spread of either NO3¯ or NH3 in both 2007 and 2008. This could be used as an argument that the system is in some sort of quasi-steady state, giving confidence to the use of a steady-state model. It should also be noted that Figs. 2 and 3 display the mean values of the observational data, whereas Fig. 1 shows all data as discrete data points. In all three figures, the solid black line shows the profile generated by OMEXDIA. The oxygen profile in Fig. 1 also clearly shows a burrow structure, with increased O2 concentrations in 1 profile from the SWI down to 13 mm; this may have also slightly affected the fit of the parameters. The fitted parameters led to interpretable model profiles typical of the system studied.

 The values of each parameter after being fitted by the μGA are shown in Table 1, along with parameter values from the original OMEXDIA model. The values for the five most sensitive parameters show relatively sensible values (e.g. an increase in the bioturbation coefficient from 0.0027 cm2 d-1 to 0.047 cm2 d-1 seems realistic considering the difference in benthic biological activity between low productivity continental slopes and relatively high productivity shallow coastal seas). The estimated bioturbation coefficient also resembles the values derived from experimental work, as shown in Table 1. More surprising is the value of the mean POC flux to the sediment of 16 g C m-2 yr-1. Compared to previous estimates of carbon fluxes in the North Sea, this is particularly low, with ranges given in the literature for high productivity areas being between 31 and 130 g C m-2 yr-1 (de Haas and van Weering 1997; Anton et al. 1993; Gargas et al. 1980). However, this could again be explained by the fact that the majority of the fast degradable carbon is mineralised in the water column; if the carbon flux to the benthic fluff layer could be measured, it would likely promote higher values comparable to previous estimates.

 Although all parameter values generated by the genetic algorithm are listed in Table 1, it should be noted that care is needed when attempting to interpret these values. The vast majority of parameters in the model are derived from the Monod kinetics of the model formulation (Boudreau 1997), and are parameters that are not routinely measured during observational work. In particular, the half-saturation constant values represent the concentration of the oxidant which can carry out the reaction at 50% of the fastest theoretical rate; the only method to obtain values for these parameters is to fit experimental data to model output. It is therefore difficult to make comparisons of the values of these parameters between different environments (e.g. sediment composition, water depth etc.). Other parameters, such as the rates of the reactions, do have a more tangible meaning, and it is relatively easy to make comparisons between them and the values obtained in experimental situations. For example, degradation of bacterial matter has been studied with results ranging from 0.002 to 0.101 d-1 in oxic coastal environments (Huettel et al. 2007; Westrich and Berner 1984; Jensen et al. 2005; Andersen 1996; Sun et al. 1991); although the μGA result of 0.0576 d-1 for fast-degrading organic matter has to be in the range given to the algorithm, the literature range is relatively large and a final value of 0.0576 d-1 implies that the North Dogger site is a particularly active biogeochemical environment; given that previous experimental work has tended to concentrate more on highly labile organic matter, a μGA result of 0.0001 d-1 for slow degrading organic matter also seems reasonable.

 The μGA generated values for five parameters which were outside of the range found in the literature. Three of these parameters were diffusion coefficients (oxygen, nitrate and ODU). The ODU diffusion coefficient in Table 1 was compared with the diffusion coefficients for the constituent components of ODU (Mn2+, Fe2+ and S2-), and so it is difficult to compare these like-for-like. The optimised value for the oxygen diffusion coefficient was slightly larger than the values reported in the literature, by 0.36 mmol m-2 d-1, while the optimised nitrate diffusion coefficient was smaller than the lowest literature value by 0.38 mmol m-2 d-1. Given that the literature range for the oxygen diffusion coefficient is very small, and only from one study in a brackish estuary, and the range for the nitrate diffusion coefficient is 2.59 mmol m-2 d-1, the values generated by the algorithm seem reasonable. The value of advection generated is only 6% lower than the range given in the literature, and so again this seems a reasonable value particularly given the discussion regarding the difference between *advection* and *sedimentation rate* in Note *f* of Table 1. However, the value of the NH3 adsorption coefficient generated is 6.8 times larger than the largest literature reported value for the algorithm using just 2007 data. Although this is a large difference, the range in the literature is from just one study; it is noted in Mackin & Aller (1984) that temperature will have an effect of up to 25% over a 20°C range; it is also noted that high porosity (i.e. sandy) sediments will lead to low adsorption coefficients. It is unknown what effect very low porosity sediments will have, and this is a clear area where further research would help validate the model output. For brevity, a discussion of all remaining parameters is not necessary; however, as shown in Table 1, the results provided by this μGA technique does provide a full set of parameter values that are sensible when compared with observational data.

 The results here show that, despite the complexity of OMEXDIA, it is possible to calibrate it against data from a different environment for which it was designed, and that a robust validation can be accomplished using a separate set of observations from a similar environment (see Fig. 3). In the case shown here, the data used for validation was from the same location but a different period of time as the data used for calibration. Figure 3 also shows that by changing the values of just three model parameters (oxygen, nitrate and ammonia bottom water values), accurate profiles can be generated. These results, showing that correct profiles can be generated for a different set of data, shows the robustness of both the model and the μGA technique.

 Giving the model values for other parameters for which values can be found empirically (such as the C:N ratio, and an estimate of the proportion of refractory carbon in the system) may enable a validation run to have a closer agreement with the observed data. Further research would need to be carried out to find out if the values found for the remaining parameters using the μGA method are also valid for other locations in the North Sea. However, given the highly dynamic nature of shelf-sea systems, it is likely that more suitable parameter values would need to be found and therefore a new calibration would need to be carried out for each location.

 It is recognised that this work gives detailed results from only one study site. However, future work will allow us to determine whether the parameters generated in this study can be used in a predictive manner, both across different sedimentary environments that are geographically close, and in similar sedimentary environments in different marine areas. However, as this study shows, μGA techniques are a potentially valuable method in generating parameter values that are otherwise difficult to obtain and, as such, are a means towards explaining the processes that may are occurring in complex environments such as coastal marine sediments.

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**Table 1** Table to show list of parameters used in the model, default values, results of sensitivity analysis and values of each parameters obtained from the best fitting result of Experiments 1 and 2 (see main text for details of this experiment)

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  |  |  | Ranges of valuesb |  |  |  |  |
| **Parameter** | **Units** | **Default valuesa** | **Lower value** | **Upper value** | **Overall rankc** | **GA output (all data)d** | **GA output (2007 data)** | **Comparisonse** |
| Mean carbon flux to the sediment | g C m-2 year-1 | 20 | 2 | 100 | 1 | 19.1 | 16 | 31-130 1-3 |
| O2 in overlying bottom water | mmol O2 m-3 | 300 | 248 | 300 | 2 | 248.27 | 248.27 | - |
| Nitrogen to Carbon ratio in fast degrading organic matter | moles N : moles C | 0.16 | 0.14 | 0.16 | 3 | 0.14 | 0.14 | 0.05-0.3 4-7 |
| NH3 in overlying bottom water | mmol NH3 m-3 | 1 | 0.1 | 0.54 | 4 | 0.54 | 0.25 | - |
| Bioturbation coefficient | cm2 day-1 | 0.003 | 0.002 | 0.15 | 5 | 0.044 | 0.039 | 0.0002-0.2 5,8-10 |
| Rate of nitrification | day-1 | 20 | 2 | 200 | 6 | 49.14 | 90 | 0.86-143 11,12 |
| Proportion of fast degrading organic matter | - | 0.9 | 0.001 | 0.999 | 7 | 0.952 | 0.730 | - |
| O2 diffusion coefficientg | cm2 d-1 | 1.34 | 1.15 | 1.53 | 8 | 1.22 | 1.19 | 0.67-0.86 13 |
| NO3¯ in overlying bottom water | mmol NO3¯ m-3 | 10 | 0.1 | 6.42 | 9 | 1.5 | 0.1 | - |
| NH3 diffusion coefficientg | - | 1.18 | 1.01 | 1.35 | 9 | 1.01 | 1.25 | 0.432-4.32 14-19  |
| Nitrogen to Carbon ratio in slow degrading organic matter | moles N : moles C | 0.13 | 0.08 | 0.13 | 11 | 0.13 | 0.11 | 0.05-0.3 4-7 |
| Rate of oxidation of fast degrading organic matter | day-1 | 0.01 | 0.001 | 0.1 | 11 | 0.097 | 0.1 | 0.002 to 0.101 20-24 |
| Oxygen demand units diffusion coefficient | - | 1.08 | 0.963 | 1.21 | 13 | 1.202 | 1.079 | 0.328-0.536 18,25,26 |
| NO3¯ diffusion coefficientg | - | 1.18 | 1.01 | 1.35 | 14 | 1.35 | 1.35 | 1.73-4.32 14,27,28 |
| Half-saturation concentration of NO3¯ in denitrification | mmol NO3¯ m-3 | 30 | 3 | 300 | 15 | 106.7 | 64.29 | - |
| Rate of oxidation of oxygen demand units | day-1 | 20 | 0.1 | 10 | 16 | 0.57 | 2.14 | - |
| Half-saturation concentration of O2 in nitrification | mmol O2 m-3 | 1 | 0.1 | 100 | 17 | 100 | 4.9 | - |
| Advection ratef | cm day-1 | 2.74x10-7 | 2.74x10-8 | 2.74x10-6 | 18 | 2.39x10-6 | 2.14x10-6 | 6.85x10-5 – 1.10x10-3 1,20,21 |
| Rate of oxidation of slow degrading organic matter | day-1 | 1x10-5 | 1x10-6 | 1x10-3 | 19 | 4x10-4 | 1x10-3 | 0.002 to 0.101 27,28,33 |
| Mixed layer depth | cm | 5 | 0.5 | 15 | 20 | 15 | 9.0 | 2-20 2,8,9 |
| Half-saturation concentration of NO3¯ inhibiting anoxic mineralisation | mmol NO3¯ m-3 | 1 | 0.1 | 10 | 21 | 7.96 | 4.50 | - |
| Half-saturation concentration of O2 in oxidation of ODU | mmol O2 m-3 | 1 | 0.1 | 10 | 22 | 9.37 | 10 | - |
| Half-saturation concentration of O2 in inhibiting denitrification | mmol O2 m-3 | 1 | 0.1 | 10 | 22 | 10 | 10 | - |
| Half-saturation concentration of O2 in oxic mineralisation | mmol O2 m-3 | 3 | 0.3 | 30 | 24 | 29.1 | 30 | - |
| NH3 adsorption coefficient | - | 1.3 | 0.13 | 13 | 25 | 8.71 | 13 | 0.8-1.9 29 |
| Half-saturation concentration of O2 inhibiting anoxic mineralisation | mmol O2 m-3 | 1 | 0.1 | 10 | 26 | 0.73 | 0.1 | - |

a Default values in OMEXDIA (Pers. comm. K. Soetaert)

b Range of values of parameters used in sensitivity analysis experiment and in Experiment 2 of the μGA

c Overall rank determined after sensitivity analysis experiments

d The value of the parameter given by the best fitting genetic algorithm output

e Values aren’t given where the parameters are formulated purely for the model (*e*.*g*. half-saturation constants). Values are also duplicated where experimental work is unable to separate values between separate model parameters (*e*.*g*. differentiating between fast and slow degrading organic matter)

f diagenetic models tend to use the term ‘advection rate’, whereas experimental work often measures only ‘sedimentation rate’. Given the lack of data in the literature for ‘advection rates’, for the purposes of comparison here, they are treated as the same parameter so that they can be compared like-for-like (the values shown in the ‘comparisons column’ are reported ‘sedimentation rates’). However, sedimentation only takes into account that material which is accumulated at the sediment-water interface. Advection would normally be interpreted as a function of depth that not only considers sedimentation, but also the impact of compaction that will occur throughout the sediment column. However, in OMEXDIA, advection is a depth-independent parameter, with units of cm d-1. Given that sedimentation rate will include organic matter which will be degraded, whereas advection will be the integrated rate over the whole sediment column, it is not surprising that sedimentation rate is higher than advection rate.

 g n.b. For diffusion coefficients, values have been compared directly with values cited; the coefficient hasn’t been compared with theoretical DTs (i.e. calculated using equations in Li & Gregory (1974) using T from the papers cited)

1 de Haas & van Weering (1997)

2 Anton et al. (1993)

3 Gargas et al. (1980)

4 Jossain et al. (2011) – n.b. this N:C ratio is in water column OM

5 Beck et al. (2009)

6 Rusch et al. (2000)

7 Van Cappellen & Wang (1996)

8 Mouret et al. (2009)

9 Arndt & Regnier (2007)

10 van der Zee et al. (2002)

11 van Raaphorst et al. (1990)

12 Smits (1980)

13 Revsbech et al. (1980)

14 Rutgers van der Loeff (1980)

15 Kamiyama et al. (1976) – n.b. sediment temperatures not given

16 Emerson et al. (1984)

17 Aller (1980)

18 Krom & Berner (1980)

19 Li & Gregory (1974)

20 Epping et al. (2002)

21 van Weering et al. (1987)

22 Andersen (1996)

23 Huettel et al. (2007)

24 Westrich & Berner (1984)

25 Goldhaber et al. (1977) n.b. sulphate values used to represent ODU

26 Iversen & Jørgensen (1993)

27 Vanderborght & Billen (1975)

28 Jensen et al. (2005)

29 Mackin & Aller (1984)

**Figure Captions:**

**Fig. 1** Fitted model output (solid line) and all available experimental data (open circles) from the best fitting profiles of Experiment 1, showing the mean and standard deviation (dashed lines) of the experimental data

**Fig. 2** Best fitting profiles from Experiment 2, using only 2007 data to fit model output. Note that the profiles show the mean concentrations from multiple cores from each cruise

**Fig. 3** Model output profiles from Experiment 3, with 2008 observational data. Note that the profiles show the mean concentrations from multiple cores from each cruise

