

REC_v3 - Users manual

Karsten Lettmann

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1 Introduction

In marine biogeosciences, it is a common problem to determine nutrient consumption and production rates along vertical sections through the water column or in the underlying sea-floor sediments. On the basis of these consumption and production rates, it is for example possible to identify zones with high biological activity along the considered vertical transects.

The drawback with the consumption and production rates is that it requires a lot of work to determine these rates. Therefore, it is common practise to estimate these nutrient consumption and production rates from measured vertical concentration profiles of the respective nutrients like O_2 or SO_4^{2-} , which are more easily to access.

In order to determine consumption and production rates under steady state conditions, the following equation can be considered, which relates the nutrient concentration with processes of sedimentation, pore water advection, molecular diffusion, bioturbation, irrigation and the valid consumption and production rates (for more details concerning this equation, see e.g. Boudreau [1997] or Berg et al. [1998]):

$$\frac{d(\phi w C)}{dz} - \frac{d}{dz} \left(\phi (D + D_B) \frac{dC}{dz} \right) + \phi \beta (C - C_W) = R \quad (1)$$

Here, C denotes the nutrient concentration and R the valid consumption and production rate. Furthermore, ϕ denotes the sediment porosity, w the sedimentation rate combined with pore water advection, D the molecular diffusion coefficient (corrected for sediment properties), D_B denotes the bioturbation coefficient, β the coefficient of irrigation and C_W the nutrient concentration in the water column right above the sediment.

These coefficient function can be constant over the considered depth interval or could be depth-dependent. In addition, this equation is also valid in the water column, if sediment porosity is set to $\phi = 1$ and the processes of bioturbation and irrigation are neglected.

The REC_v3 (**R**ates **E**stimation from nutrient **C**oncentration profiles) calculates consumption and production rates on the basis of nutrient concentrations. It solves an inverse linear system via a technique called Tikhonov regularization, and is delivered in five subfolders:

- **manual**: This folder contains this manual.
- **matlab_code_with_GUI**: This folder contains the MATLAB program version which can be controlled via a graphical user interface. Similarly, MATLAB must have been installed.
- **windows_executable**: This folder contains the windows executable version, which can be executed without MATLAB, if the MGL toolbox has been installed. This windows executable has been build from the MATLAB code via the MATLAB compiler.
- **MGL**: This folder contains a MATLAB related toolbox, which must be installed first, if the windows executable is to be used.

2 The numerical algorithm

From equation (1), an inverse linear system is build via discretization of the continuous derivatives on a computational grid. This inverse system is solved with a technique called *Tikhonov regularization*, which can find relatively stable solutions in the presence of measurement errors. The different steps of the algorithm are depicted in Fig. 10:

In the first step, the nutrient concentration data and the coefficient functions (e.g. porosity, the diffusion coefficients etc.) must be provided to the numerical algorithm via text files.

In second step, the possibly irregular distributed nutrient concentration data and the coefficient functions are interpolated to a regular spaced computational grid. With these regularly spaced data, the inverse linear system is build in the third step.

In the fourth step, this inverse linear system is solved via Tikhonov regularization. For this technique, two stabilizing parameters must be defined, which control the smoothness of the final rate profile. The first parameter λ (called the 'smoothing' parameter) must be set by the user, while the second parameter α (Tikhonov parameter) is determined via an numerical procedure. For this procedure, the user must provide the boundaries of the interval, in which the optimal α is searched for. During this finding process of the optimal α , local minima of the so-called *ratio-criterion*

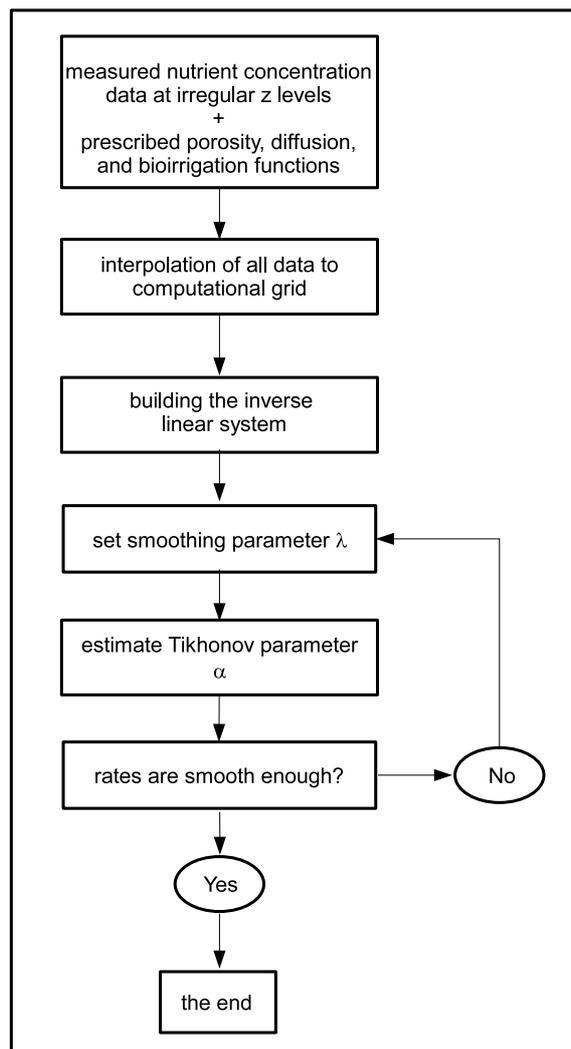


Figure 1: Sketch over the numerical procedure.

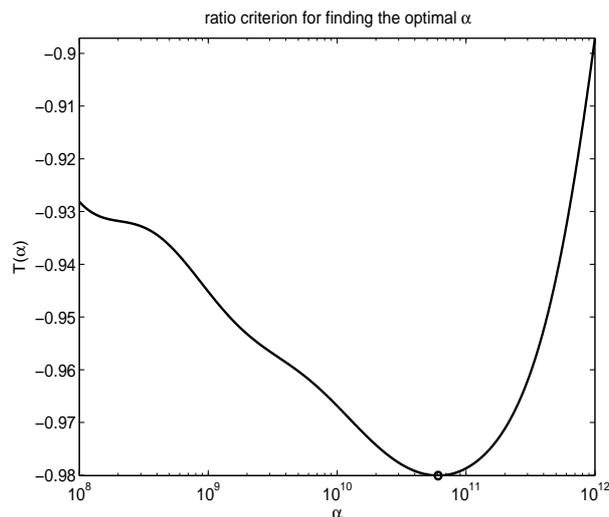


Figure 2: Example of the ratio criterion $T(\alpha)$ for finding an 'optimal' Tikhonov parameter α .

are searched for. In Fig. 11 an example of this ratio-criterion function can be seen. Here, the circle marks the optimal α , which will be used finally for the Tikhonov regularization. On this figure, the optimal α parameter is searched for in the interval 10^8 to 10^{12} .

The value of the smoothing parameter λ influences the smoothness of the obtained rate function. If this parameter is very large, the rate function will be very smooth with nearly no extreme maxima and minima, or will even be a straight line.

In the last step, the calculated rate function is plotted on the screen and the results are printed to an output file.

If the obtained rate profile is not smooth enough or too smooth, the user could change the smoothing parameter λ accordingly, and could start the model, again.

3 How to use the model

3.1 Installing the numerical model

Please extract the zip-archive to a working folder of your choice. If the MATLAB code is to be used, the model is ready to use, if MATLAB is installed on the computer.

If the windows executable is to be used, the MGL toolbox must be installed, first. To install the MGL toolbox, change to the MGL folder and execute the *mglinstaller.exe* file, which starts the installation process. During the process you will be asked to provide the name of a folder where to install the MGL toolbox. Please press only the *Enter* button, to install the toolbox in the current folder. If the installation is successful, the windows executable is ready to use.

3.2 Preparing the setup folder and the input files

The procedure to model a new nutrient concentration profile is similar to for all model versions. Change to the folder with the model version to use (MATLAB, MATLAB with GUI, or the windows executable) and create a new folder. In this example, the name of the setup folder is marked by the * symbol.

After creating the setup folder, simple ascii files must be created containing the profiles of the nutrient concentration and the coefficient functions. These files must be located in the setup folder and must start with the name of the setup folder. In total, six different files must be created each consisting out of two columns. The first column contains the depth levels and the second column the respective property. In the following table, the necessary files with their file endings are listed.

property	file end
nutrient concentration C	*_C.txt
porosity ϕ	*_phi.txt
vertical advection velocity ω	*_omega.txt
effective molecular diffusion coefficient D	*_D.txt
bioturbation coefficient D_B	*_Db.txt
irrigation coefficient β	*_beta.txt

In this table, the * symbol stands for the setup name.

The depth interval of the setup is determined by the depth interval set by the concentration input file via the first and the last depth level. Therefore, the first and the last depth level in the other five input files must be equal. If this is not the case, an error message will appear during the execution of the program.

While the nutrient concentration is usually depth dependent, the coefficient functions might be constant over the considered depth interval. An easy way to prescribe a constant coefficient function is to provide the constant value at the top and at the bottom depth level. If, for example, a constant porosity of 0.75 is assumed over a depth interval from 0 cm to 50 cm, the *_phi.txt file should look like:

```
0.0  0.75
50.0 0.75
```

At depth levels not given in the input file, the values of the coefficient functions are determined by linear interpolation. If, for example, a profile of the effective diffusion coefficient is assumed, which is linear decreasing in the first 20 cm of the sediment from a value of $3.0 \cdot 10^{-5} \text{ cm}^2/\text{s}$ to $1.0 \cdot 10^{-5} \text{ cm}^2/\text{s}$, and which is constant over the

next 50 cm, the *_D.txt file should look like:

```
0.0  3.0e-5
20.0 1.0e-5
70.0 1.0e-5
```

During the execution of the program, the six input profiles are depicted in two figures, each consisting out of three subfigures. With the help of these figures, the user can verify, whether the input functions used for the computational process are correct.

3.3 Starting the model

3.3.1 Running the MATLAB code with the graphical user interface

To use the MATLAB code with the graphical user interface, please start MATLAB on your computer and change the current MATLAB working directory to the folder 'matlab_code_with_GUI'. The model is started by executing the m-file REC_v3_with_GUI.m.

3.3.2 Running the windows executable

To use the windows executable, the MGL toolbox must have been installed, which is described in section 3.1. If that is the case, please change to the folder 'windows_executable'. The program is started by double-clicking on the batch-file run_REC_v3.bat.

3.4 Providing the input parameters to the model

3.4.1 Using the graphical user interface

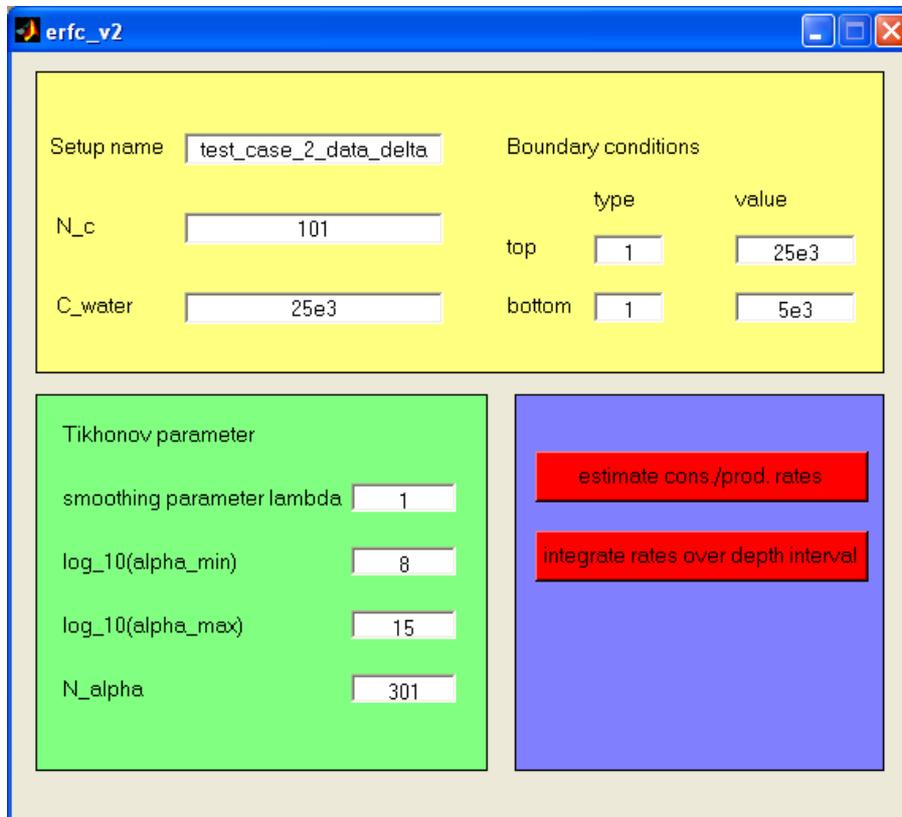
If the windows executable or the MATLAB code with graphical user interface is to be used, the necessary input parameters are provided via a graphical window, which is depicted in Fig. 3. Via this window, the user must provide the setup name, the size of the computational grid, the water nutrient concentration in the case of irrigation, the boundary conditions for the nutrient concentration, and the parameters used for the Tikhonov regularization. Now, these input parameters will be described in more detail.

setup name Here, the name of the setup folder must be provided, which has been explained in section 3.2.

N_c Number of used control levels, which is equal to the number of the computational grid points. This number should be higher than the number of the nutrient concentration data values.

C_{water} If irrigation is considered, the nutrient concentration in the water column above the sediment surface must be provided. The unit should be μM .

boundary conditions Here, the user must provide information about the nutrient boundary conditions at the top and bottom of the considered depth interval. The 'type' switch can be 1 or 2. In the case of Dirichlet boundary conditions (the nutrient concentration value is fixed), 'type' must be set to 1. In case of



The screenshot shows a window titled 'erfc_v2' with a yellow background. It contains several input fields and buttons. The 'Setup name' field is 'test_case_2_data_delta'. The 'Boundary conditions' section has a table with 'type' and 'value' columns. The 'Tikhonov parameter' section has fields for 'smoothing parameter lambda', 'log₁₀(alpha_min)', 'log₁₀(alpha_max)', and 'N_alpha'. The 'estimate cons./prod. rates' and 'integrate rates over depth interval' buttons are red.

	type	value
top	1	25e3
bottom	1	5e3

Parameter	Value
smoothing parameter lambda	1
log ₁₀ (alpha_min)	8
log ₁₀ (alpha_max)	15
N_alpha	301

Figure 3: The graphical user interface to provide the necessary input parameters. Here, all the parameters correspond to the provided example test case.

von Neumann boundary conditions (the derivative of the nutrient concentration is given) 'type' must be set to 2. Nutrient concentration units must be μM , whereas derivatives are given in $\mu\text{M}/\text{cm}$. For 'value', the corresponding numerical value must be given.

Tikhonov parameter Here, the necessary parameters for the Tikhonov regularization are provided. The user must provide the value of the smoothing parameter λ , and the range of the α parameter, where the boundaries are given as exponents to the basis of ten. In other words, the optimal α is searched for in the interval $\alpha_{min} = 10^{p_{min}}$ and $\alpha_{max} = 10^{p_{max}}$. Finally, N_alpha denotes the number of the tested optimal α in the given interval. If this number is only two, only the left and right boundary value is tested. If this number is large (around 500) the given α -interval is sampled in more detail.

Furthermore, it might be necessary to change the boundary values for the α parameter in several model runs, to find an optimal local minimum of the ratio-criterion function.

3.5 The model output data

Estimate rates - button Having provided the input data and pressing the button 'estimate cons./produc. rates' the consumption and production rates are calculated from the input data. Furthermore, three output files are generated, which are located in the setup folder and which are named:

- * **_output.txt** This file contains the estimated profile of the consumption and production rates and the fitted nutrient concentration.
- * **_output.jpg** The figure of the estimated results.
- * **_output_fluxes.txt** This file contains the diffusive and advective fluxes across the interfaces of the considered depth interval. These fluxes are calculated from the fitted concentration profile via:

- diffusive flux : $-\phi(D + D_B)\frac{dC}{dz}$
- advective flux : $\phi\omega C$
- total flux : sum over diffusive and advective flux

Integrate rates - button After the consumption and production rates have been calculated, the user can integrate the rate profile over a selected depth interval. To do this, the button 'integrate rates over depth interval' must be pressed.

Then, the figure 4 opens again, and the user must select via the computer mouse, the two depth levels over the rate profile. After the two depth levels have been selected, the rates are integrated over that interval via Simpson's rule. The result of this integration is written to the file '*_output_rate_integration.txt'.

4 An example test case

The test case considers a consumption rate with a larger consumption peak near the surface of the sediment and a smaller consumption peak in a deeper sediment layer with the following rate function:

$$R(z) = -4.0 \cdot 10^{-4} \frac{\text{nmol}}{\text{cm}^3 \text{s}} e^{-(z-10 \text{ cm})^2/10 \text{ cm}} \\ -2.0 \cdot 10^{-4} \frac{\text{nmol}}{\text{cm}^3 \text{s}} e^{-(z-40 \text{ cm})^2/10 \text{ cm}}$$

Sedimentation, bioturbation and bioirrigation are neglected ($\omega = 0$, $D_B = 0$ and $\beta = 0$), and the other coefficient functions are constant with $\phi = 0.75$, $D = 0.685 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. The nutrient concentration boundary conditions at the top and bottom are $C_{top} = 2.5 \cdot 10^4 \mu\text{M}$ and $C_{bottom} = 0.5 \cdot 10^4 \mu\text{M}$. The profile of the consumption rate R and the resulting concentration profile C is depicted in Fig. 4.

From this rate function and the coefficient functions, the resulting nutrient concentration is calculated by solving the differential equation (1) numerically. To the obtained nutrient concentration random noise was added to simulate some measurement errors. The prepared input files are stored in the test case folder with the name 'test_case_2_data_delta'.

The used input parameters for the model run are shown in Fig. 3. If the model is started, the input profiles are depicted in the first to appearing figures. For the considered test case, these figures are shown in Fig. 5 and 6.

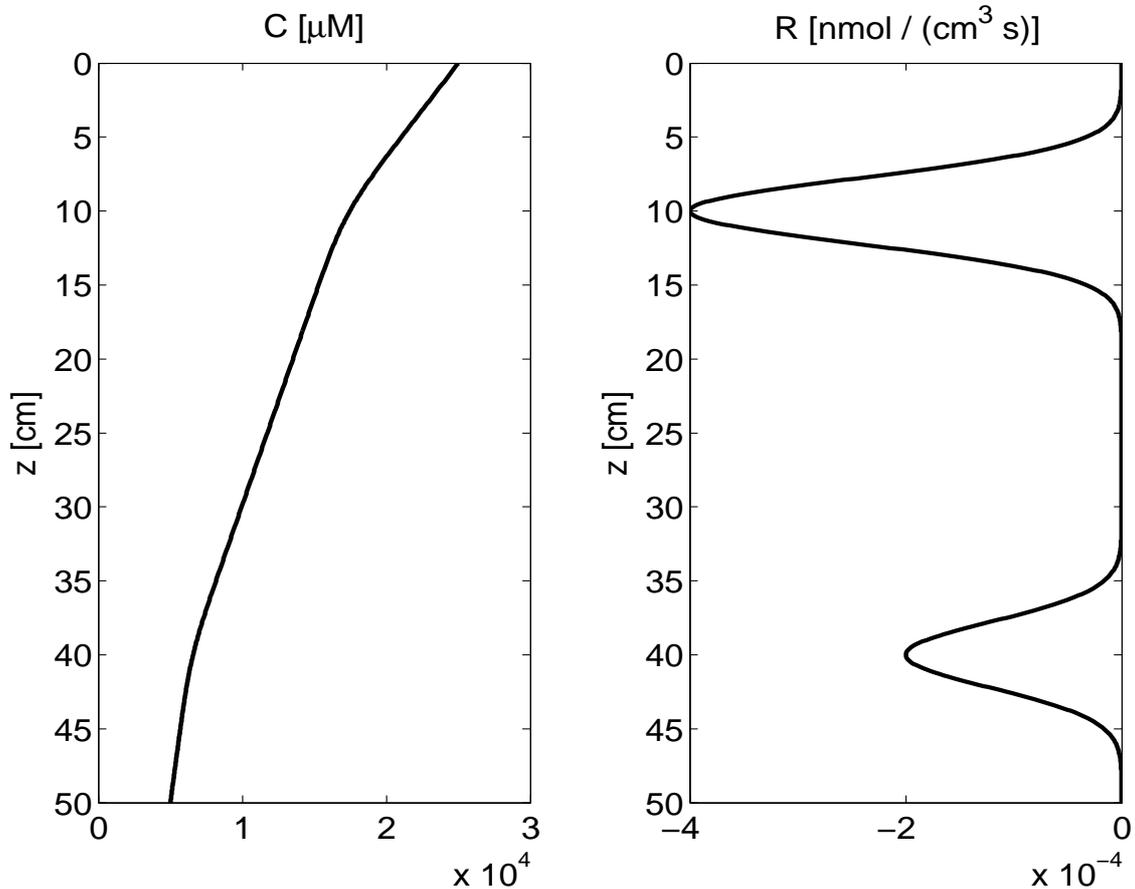


Figure 4: The profile of the consumption rate R and the resulting concentration profile C for the considered test case.

Furthermore, Fig. 7 shows the obtained ratio criterion function, where the black circle denotes the optimal α taken for the Tikhonov regularization. Finally, using a smoothing parameter $\lambda = 1$, the resulting rate function is depicted in Fig. 8.

If a larger smoothing parameter $\lambda = 100$ is used, one gets the result shown in in Fig. 9. In that case, the obtained rate function is much smoother, with minor peaks.

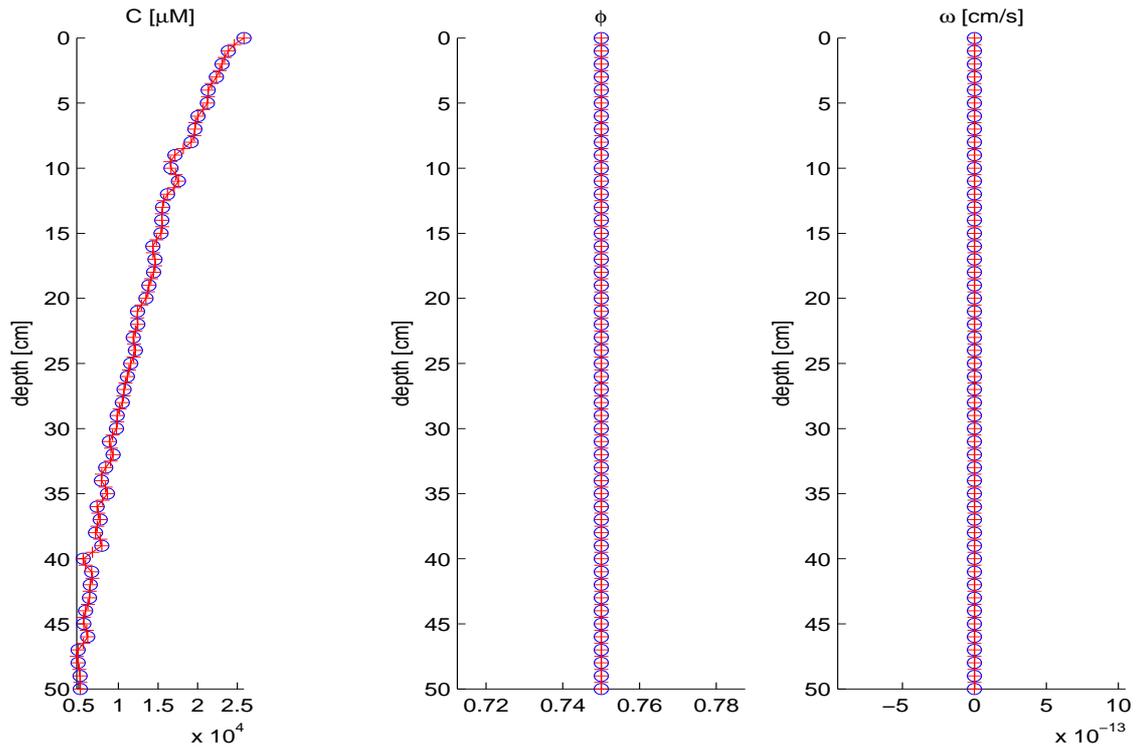


Figure 5: The first figure after starting the model, which depicts the input profiles of the nutrient concentration, the porosity and the sedimentation rate. In this test case, porosity and sedimentation rate are constant over the considered depth interval.

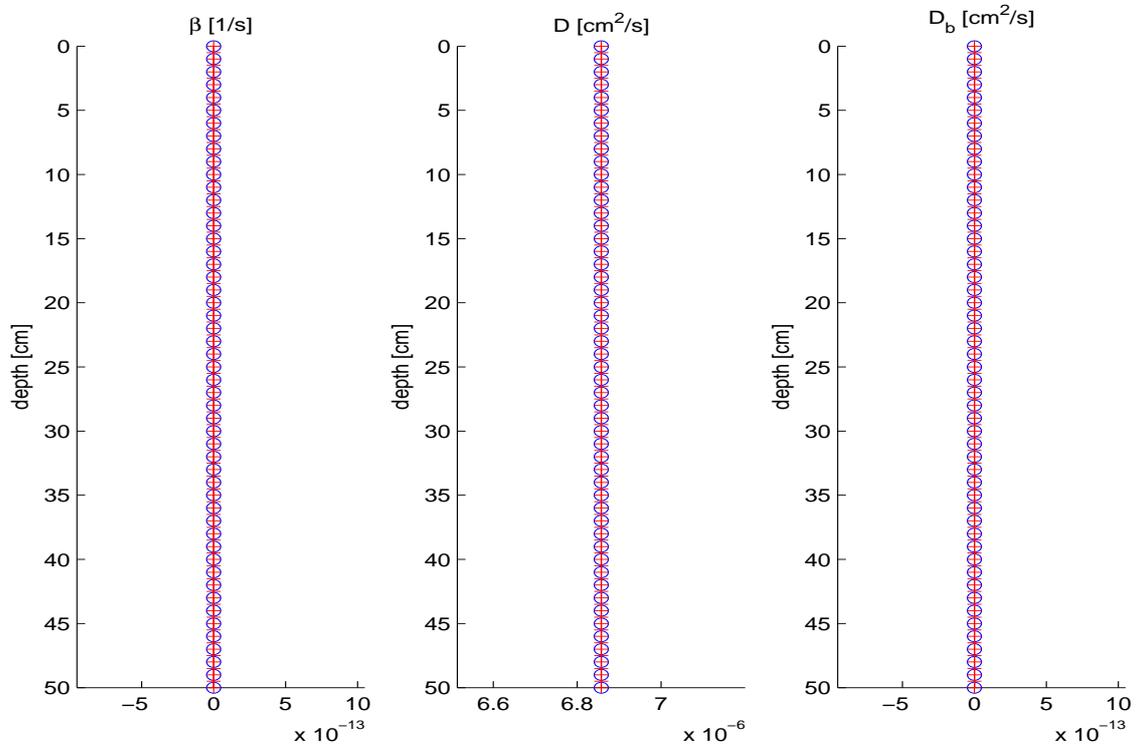


Figure 6: The second figure after starting the model, which depicts the input profiles of the irrigation coefficient, the molecular diffusion coefficient, and bioturbation coefficient. In this test case, irrigation and bioturbation are neglected, and molecular diffusion is set constant over the considered depth interval.

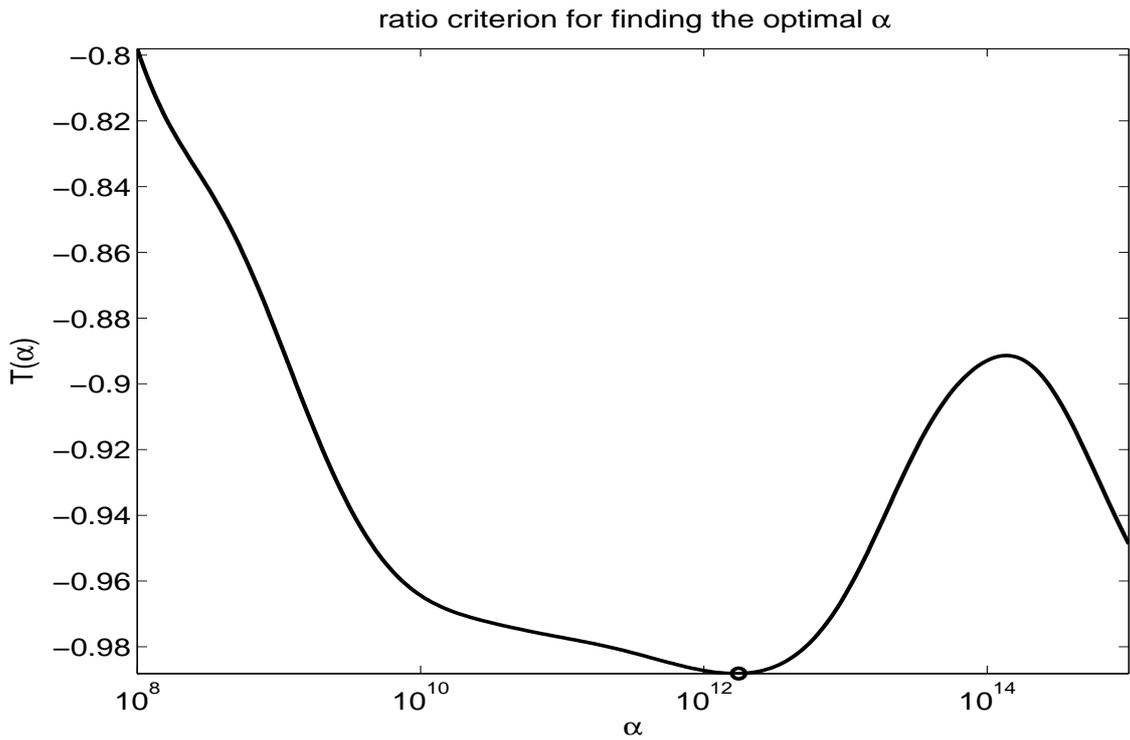


Figure 7: The obtained ratio criterion function for the considered test case. The black circle marks the optimal α .

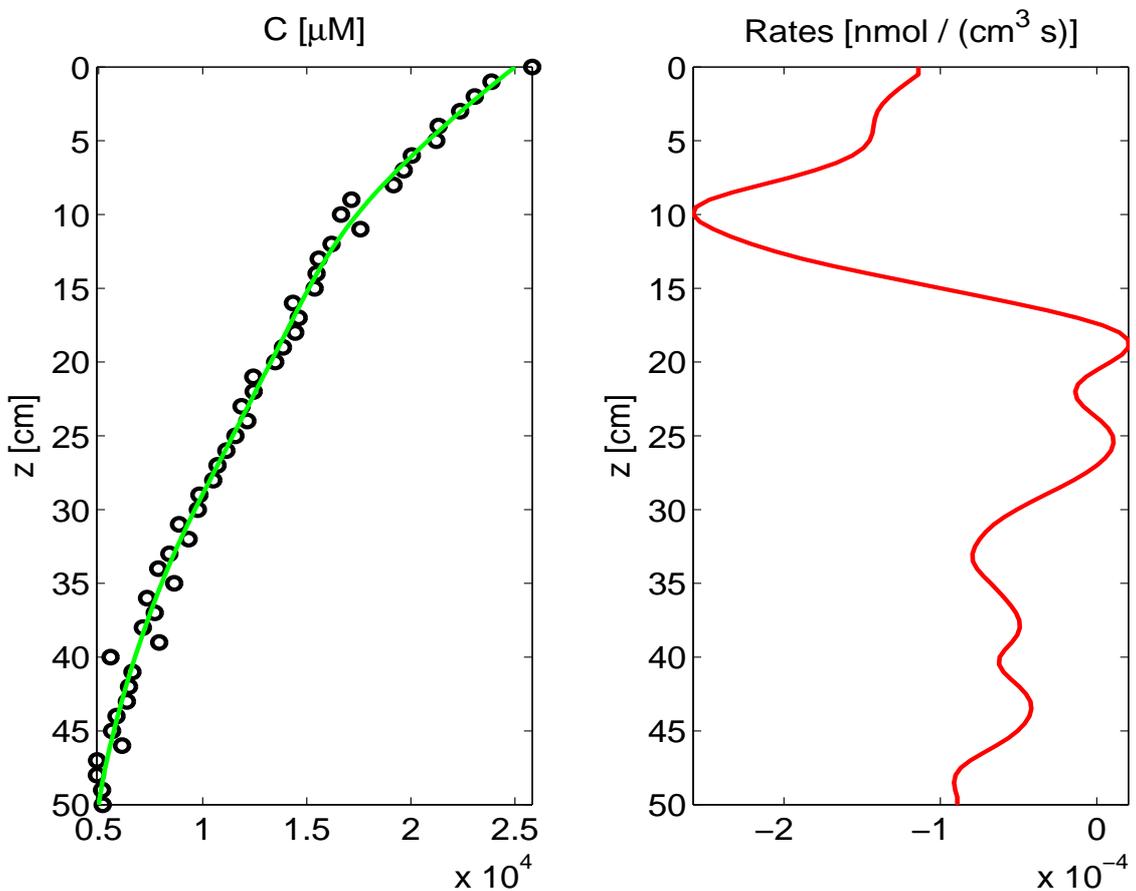


Figure 8: Result obtained with the given input parameters shown in Fig. 3 using a smoothing parameter $\lambda = 1$.

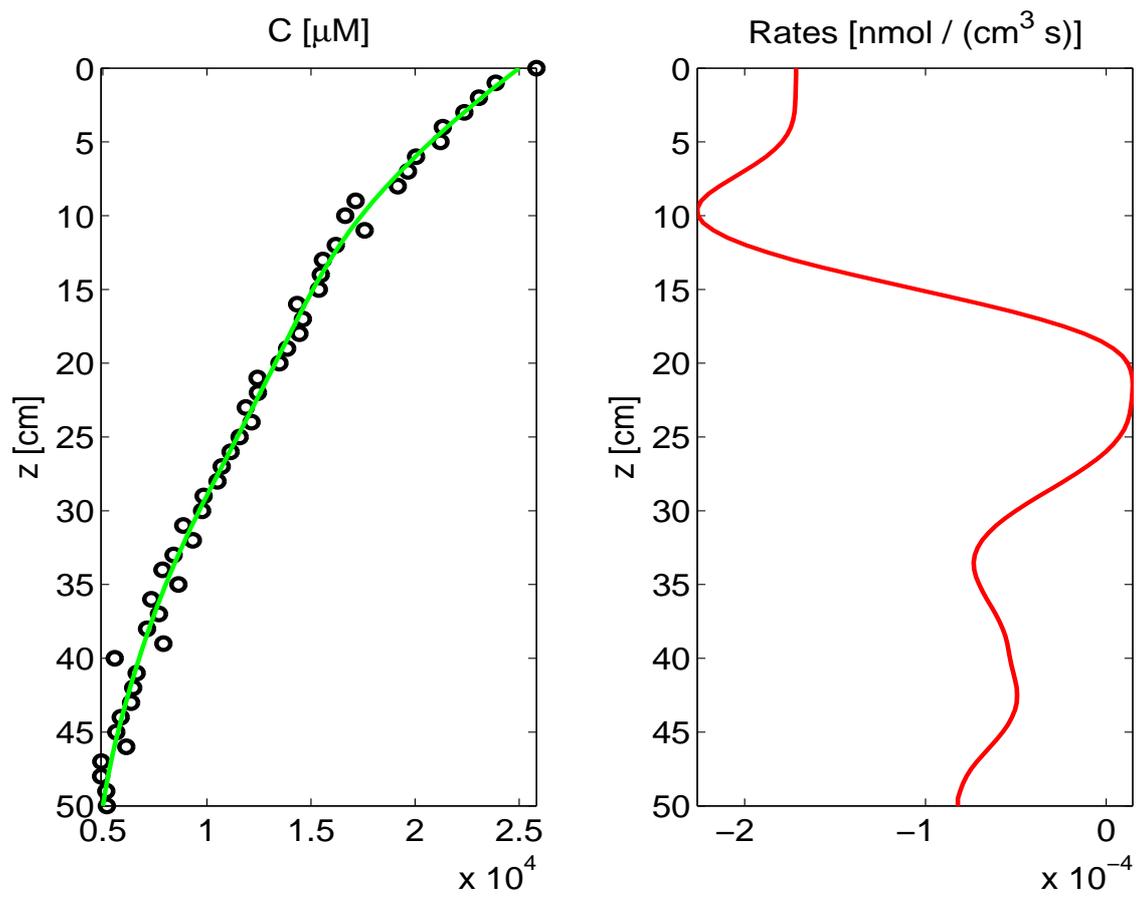


Figure 9: Result obtained with the given input parameters shown in Fig. 3 using a smoothing parameter $\lambda = 100$.

A Numerical Technique

Here, the numerical procedure is to be explained in more detail. This is a very preliminary version of the technical documentation - so be careful !!

On overview of the numerical procedure is depicted in the flow chart in Fig. 10. Although it might look complicated at the first glance, it contains the necessary steps and relations between all the different quantities and additional profiles, which are calculated during the procedure. This flow chart can be used as a map to find the right path in the 'jungle' of the proposed method.

Before, each step of this flow chart is explained in more detail, a short overview: As mentioned in section ??, the basic step of the procedure is building the stabilizing matrix $\underline{\mathbf{H}}$, which is a combination of the original finite difference approximation of the basic differential equation (1) and some additional stabilizing terms, by means of a technique called Tikhonov regularization (see e.g. Engl et al. [2000], Björk [1996], or Hofmann [1999]). In order to construct this matrix $\underline{\mathbf{H}}$, two free parameters have to be provided, of which the Tikhonov parameter α can be estimated via an objective criterion. This parameter selection process is denoted by the central gray-shaded box in the middle of the flow chart. Furthermore, the matrix $\underline{\mathbf{H}}$ is not directly applied to the concentration data. Instead, first, the concentration data have to be interpolated to a regular computational grid, and after that, a mean concentration profile is subtracted. The matrix $\underline{\mathbf{H}}$ is applied to the residual concentration data ($\tilde{\mathbf{C}}_r$).

A.1 Interpolation onto a Computational Grid

A very important step of the proposed numerical procedure is to provide the solute concentration data and all the coefficient functions on a discrete equidistant computational grid z_i , $i = 1, \dots, N$, where the first value, z_1 is the nearest point to the sediment surface and the last value, z_N , denotes the deepest depth value. The constant distance between the grid points is denoted by $\Delta z := z_{i+1} - z_i = \text{const.}$ for $i = 1, \dots, N - 1$. In the following, each property $f(z)$ (like solute concentrations, porosity, consumption rates, etc.) provided on this computational grid is denoted in vector notation by $\mathbf{f} = (f(z_1), \dots, f(z_N))$.

As a side remark, it is not necessary to work with a equidistant computational grid. Berg et al. [1998] built their numerical procedure on finite difference approximations applied to the irregularly sampled data points. However, due to reasons of accuracy of the finite difference approximations, we decided to use an equidistant computational grid for the finite difference approximation of the basic differential equation. The disadvantage of this decision is that the data also has to be provided on that grid, what is done by interpolation techniques. However, the reader must have in mind, that this interpolation modifies the data in some respect.

In the case of the coefficient functions ϕ , ω , D , D_B , and β , it is sufficient to use a linear interpolation technique, which draws straight lines in between the data points. In the case of the concentration input data, linear interpolation is not sufficient. This can be explained by looking at the differential equation (1). It is an ordinary differential equation of second order, and using piecewise linear approximations for the solute concentration will lead to zero rate profiles only by means of the interpolation technique.

To circumvent these problems, a cubic spline interpolation technique is used to interpolate the given concentration data onto the computational grid. By this technique, the concentration data are approximated by a series of cubic polynomials,

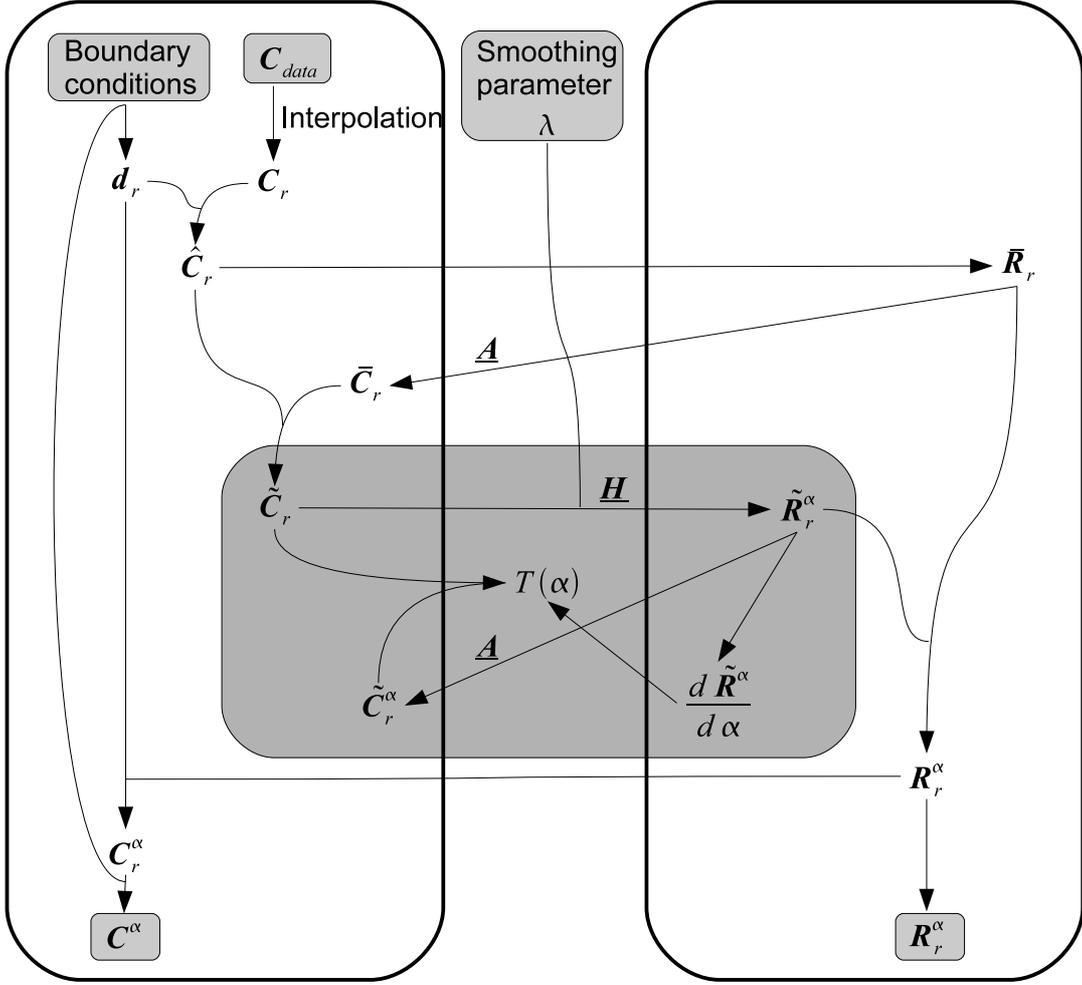


Figure 10: Flow chart of the proposed numerical procedure. The gray shaded properties at the top of this flow chart denote the input data the user has to provide. The output data of the procedure are denoted by the gray shaded boxes at the bottom of this chart. The large gray shaded area in the middle of the flow chart contains the necessary steps of estimating an optimal Tikhonov parameter α .

whose second derivatives by default are not zero. However, one has to take care about the end conditions of these cubic spline functions. It is very important not to use so called natural end conditions setting the second derivatives of the spline functions at the end points to zero. As with linear interpolation, this will by default result in zero consumption or production rates at the boundaries of the considered depth interval. Instead, so called not-a-knot end conditions should be used, which means that the cubic interpolating spline is constructed in such a way that the third derivative is continuous at the computational grid points z_2 and z_{N-1} . With such end conditions, the second derivative of the spline functions at the boundaries of the depth interval is not restricted to zero by default; and therefore, the resulting consumption and production rates are also not zero.

As a further side remark, if the data suffer from larger gaps between adjacent data points, the cubic splines might cause additional wiggles in the data gaps, which might lead to large and probably wrong estimated rate values in those data gaps. However, we have also tested spline interpolation with quadratic polynomials, which reduces the risk of additional wiggles. On the other hand, the obtained rate profiles might not be steady any more between adjacent data intervals, what is one of the major tasks of

the proposed procedure. This finally leads to the decision of using cubic splines, which produce steady rate profiles, which the risk of additional rate peaks in the cases of very irregular sampled data points.

A.2 Construction of the matrices F and A

Now, the used finite-difference approximation of the basic differential equation (1) is provided. At the start, the new quantities $\tilde{\omega} := \phi\omega$, $\tilde{D} := \phi(D + D_B)$, and $\tilde{\beta} := \phi\beta$ are defined, and the derivatives in Eq. (1) are expanded, which leads to:

$$\left[\frac{d\tilde{\omega}}{dz} + \tilde{\beta} \right] C + \left[\tilde{\omega} - \frac{d\tilde{D}}{dz} \right] \frac{dC}{dz} - \tilde{D} \frac{d^2C}{dz^2} - \tilde{\beta} C_W = R \quad (2)$$

The coefficient functions within the square brackets are combined to the following new definitions:

$$r(z) := \frac{d\tilde{\omega}}{dz}(z) + \tilde{\beta}(z) \quad (3)$$

$$s(z) := \tilde{\omega}(z) - \frac{d\tilde{D}}{dz}(z) \quad (4)$$

With these definitions, Eq. (2) can be written as:

$$r C + s \frac{dC}{dz} - \tilde{D} \frac{d^2C}{dz^2} - \tilde{\beta} C_W = R \quad (5)$$

This linear differential Eq. (5) will now be discretized on the computational grid by using finite difference approximations. The first derivatives in the functions $r(z)$ and $s(z)$ can be obtained by standard finite difference formulas on the computational grid. (See e.g. Boudreau [1997] for proper approximation formulas.)

Due to reasons of stability and accuracy, a blended approximation proposed in Boudreau [1997], which goes back to Fiadeiro and Veronis [1977], is used for the first derivative of the concentration C :

$$\left. \frac{dC}{dz} \right|_i \approx \frac{(1 - \sigma_i)C_{i+1} + 2\sigma_i C_i - (1 + \sigma_i)C_{i-1}}{2\Delta z}$$

with $\sigma_i := \coth\left(\frac{s_i \Delta z}{2\tilde{D}_i}\right) - \frac{2\tilde{D}_i}{s_i \Delta z}$

The second derivative of the concentration function is approximated by the central-difference formula:

$$\left. \frac{d^2C}{dz^2} \right|_i \approx \frac{C_{i+1} - 2C_i + C_{i-1}}{(\Delta z)^2}$$

Inserting these approximations into Eq. (5) and defining the quantities:

$$\begin{aligned} aa_i &= -(1 + \sigma_i) \frac{s_i}{2\Delta z} - \frac{\tilde{D}_i}{(\Delta z)^2} \\ bb_i &= r_i + \frac{s_i \sigma_i}{\Delta z} + \frac{2\tilde{D}_i}{(\Delta z)^2} \\ cc_i &= (1 - \sigma_i) \frac{s_i}{2\Delta z} - \frac{\tilde{D}_i}{(\Delta z)^2} \end{aligned}$$

the following relations are obtained at the grid points $i=3, \dots, N-2$:

$$aa_i C_{i-1} + bb_i C_i + cc_i C_{i+1} - \tilde{\beta}_i C_W = R_i \quad (6)$$

In the case of the grid points 1,2, N-1, and N the boundary conditions must be taken into account. For Dirichlet boundary conditions, the concentrations are fixed at the boundary points, whereas in case of von Neumann boundary conditions, the first derivative of the concentration profile is prescribed. The boundary conditions could also be mixed, with e.g. a fixed concentration at the top and a fixed first derivative of the concentration at the bottom boundary point.

To implement von Neumann boundary conditions, the following assymetric finite-difference expressions for the first derivative are used, where m_{top} and m_{bottom} denote the first derivatives at the top and bottom boundary point:

$$\begin{aligned} m_{top} &= \frac{-3C_1 + 4C_2 - C_3}{2\Delta z} \\ m_{bottom} &= \frac{3C_N - 4C_{N-1} + C_{N-2}}{2\Delta z} \end{aligned}$$

Using these expressions for von Neumann boundary conditions or taking the prescribed concentration C_{top} in case of Dirichlet boundary conditions, the following equations are obtained for the second grid point $i = 2$:

$$\begin{aligned} \text{Dirichlet:} \quad & bb_2 C_2 + cc_2 C_3 + [aa_2 C_{top} - \tilde{\beta}_2 C_W] = R_2 \\ \text{von Neumann:} \quad & \left[bb_2 + \frac{4}{3} aa_2 \right] C_2 + \left[cc_2 - \frac{1}{3} aa_2 \right] C_3 \\ & + \left[-\frac{2}{3} \Delta z aa_2 m_{top} - \tilde{\beta}_2 C_W \right] = R_2 \end{aligned} \quad (7)$$

Similarly, one obtains for grid point $i = N-1$:

$$\begin{aligned} \text{Dirichlet:} \quad & aa_{N-1} C_{N-2} + bb_{N-1} C_{N-1} \\ & + [cc_{N-1} C_{bottom} - \tilde{\beta}_{N-1} C_W] = R_{N-1} \\ \text{von Neumann:} \quad & \left[aa_{N-1} - \frac{1}{3} cc_{N-1} \right] C_{N-2} \\ & + \left[bb_{N-1} + \frac{4}{3} cc_{N-1} \right] C_{N-1} \\ & + \left[\frac{2}{3} \Delta z cc_{N-1} m_{bottom} - \tilde{\beta}_{N-1} C_W \right] = R_{N-1} \end{aligned} \quad (8)$$

These N-2 equations [one equation from (7), N-4 equations from (6) and one equation from (8)] can be written in a more compact form:

$$\underline{\mathbf{F}} \mathbf{C}_r + \mathbf{d}_r = \mathbf{R}_r \quad (9)$$

with $\underline{\mathbf{F}} \in \mathbb{R}^{(N-2) \times (N-2)}$ denoting the finite-difference matrix of the corresponding differential Eq. (5). $\mathbf{C}_r \in \mathbb{R}^{(N-2)}$ denotes the concentration vector on the interval $[z_2, z_{N-1}]$, and $\mathbf{d}_r \in \mathbb{R}^{(N-2)}$ is build from irrigation and the concentration boundary conditions. (The subscript r indicates that a vector is defined on the reduced interval $[z_2, z_{N-1}]$.) Finally, $\mathbf{R}_r \in \mathbb{R}^{(N-2)}$ denotes the rate vector on the interval $[z_2, z_{N-1}]$:

$$\mathbf{C}_r := \begin{pmatrix} C_2 \\ \vdots \\ C_{N-1} \end{pmatrix}, \quad \mathbf{R}_r := \begin{pmatrix} R_2 \\ \vdots \\ R_{N-1} \end{pmatrix}$$

If, for example, the concentration is prescribed at the top boundary and the derivative of the concentration at the bottom boundary, the vector \mathbf{d} and the matrix \mathbf{F} look like:

$$\mathbf{d}_r := \begin{pmatrix} -\tilde{\beta}_2 C_W + aa_2 C_{top} \\ -\tilde{\beta}_2 C_W \\ \vdots \\ -\tilde{\beta}_{N-2} C_W \\ -\tilde{\beta}_{N-1} C_W + \frac{2}{3} \Delta z cc_{N-1} m_{bottom} \end{pmatrix}$$

and

$$\mathbf{F} := \begin{pmatrix} bb_2 & cc_2 & 0 & \cdots & 0 \\ aa_3 & bb_3 & cc_3 & \cdots & 0 \\ \vdots & \ddots & \ddots & \ddots & \vdots \\ 0 & \cdots & aa_{N-2} & bb_{N-2} & cc_{N-2} \\ 0 & \cdots & 0 & \left(aa_{N-1} - \frac{1}{3} cc_{N-1} \right) & \left(bb_{N-1} + \frac{4}{3} cc_{N-1} \right) \end{pmatrix}$$

Defining a new modified concentration vector:

$$\hat{\mathbf{C}}_r := \mathbf{C}_r + \mathbf{F}^{-1} \mathbf{d}_r \quad (10)$$

equation (9) can be written as:

$$\mathbf{F} \hat{\mathbf{C}}_r = \mathbf{R}_r \quad (11)$$

Finally, defining the matrix $\mathbf{A} := \mathbf{F}^{-1}$, Eq. (11) can be transformed to an inverse linear system for the consumption and production rates and the modified concentration on the interval $[z_2, z_{N-1}]$:

$$\mathbf{A} \mathbf{R}_r = \hat{\mathbf{C}}_r \quad (12)$$

A.3 Estimation of the Mean Quantities

Instead of applying the Tikhonov regularization on the inverse system (12), this system is transformed into a system for the deviation profiles from specific mean quantities. In this section, the derivation of the mean quantities and their residuals is explained.

To estimate a constant mean net consumption and production rate from the measured concentration profiles and the coefficient functions two different approaches are possible. The first is based on the vertical integration of Eq. (1) over the considered depth interval. And the second approach is based on solving the linear system (12) with the a priori assumption of a constant rate data vector.

In the first approach, the constant mean rate is defined by:

$$\bar{R} := \frac{1}{L} \int_{z_{min}}^{z_{max}} R(z) dz \quad (13)$$

where $L := z_{max} - z_{min}$ denotes the length of the considered depth interval.

To obtain an estimate for this mean rate \bar{R} , the governing differential Eq. (1) is integrated over the considered depth interval:

$$L \bar{R} = \int_{z_{min}}^{z_{max}} \phi \beta (C - C_W) dz + \left[\phi \omega C - \phi (D + D_B) \frac{dC}{dz} \right]_{z_{max}} - \left[\phi \omega C - \phi (D + D_B) \frac{dC}{dz} \right]_{z_{min}} \quad (14)$$

The terms in square brackets on the right hand side denote the total element fluxes across the top and the bottom boundary of the considered interval, and the integral calculates the cumulative influence of irrigation. Although looking more difficult, the numerical estimation of this irrigation integral from measured concentration profiles is more robust and will cause only small damage to the obtained solution of the mean rate. However, the estimation of the flux terms is more problematic, because they include derivatives, whose estimation can suffer from large errors, if the measured data are very noisy.

To reduce the problems of estimating derivatives at the top and bottom of the respective depth interval, a second method can be used, which estimates the constant mean consumption and production rate from the linear system (12) on the basis of the following definition:

This mean rate is defined as that constant rate R_c , which fits best to the modified measured concentration data in a least-squares sense.

With this definition, the rate vector \mathbf{R}_r can be approximated by

$$\mathbf{R}_r \approx R_c \begin{pmatrix} 1 \\ \vdots \\ 1 \end{pmatrix} = R_c \mathbf{E}_r$$

with $\mathbf{E}_r := (1, \dots, 1)^T \in \mathbb{R}^{(N-2)}$, and the linear system (12) reduces to

$$R_c \mathbf{M} = \hat{\mathbf{C}}_r$$

where $\mathbf{M} := \underline{\mathbf{A}} \mathbf{E}_r \in \mathbb{R}^{(N-2)}$. With this equation, the *least-squares* solution for the constant rate R_c is given by:

$$R_c = \frac{1}{(\mathbf{M}^T \mathbf{M})} \mathbf{M}^T \hat{\mathbf{C}}_r \implies \bar{\mathbf{R}}_r = \begin{pmatrix} R_c \\ \vdots \\ R_c \end{pmatrix} \quad (15)$$

These two proposed constant mean rates \bar{R} and R_c need not be equal. And although the first definition seems to be more appropriate, the second definition R_c is used for the proposed numerical procedure due to its likely more robust estimation process.

Based on these mean rate $\bar{\mathbf{R}}$ a mean concentration data vector can be derived by:

$$\bar{\mathbf{C}}_r = \underline{\mathbf{A}} \bar{\mathbf{R}}_r \quad (16)$$

And with this mean concentration profile, the corresponding residual profile can be obtained:

$$\tilde{\mathbf{C}}_r = \hat{\mathbf{C}}_r - \bar{\mathbf{C}}_r \quad (17)$$

Similarly, a residual rate profile can be defined, although the rate profile \mathbf{R}_r is not known:

$$\tilde{\mathbf{R}}_r = \mathbf{R}_r - \bar{\mathbf{R}}_r \quad (18)$$

A.4 Tikhonov Regularization and the Construction of the Matrix \mathbf{H}

With the definitions of the residual profiles in Eq. (17) and (18), a linear inverse system can be constructed for these residual quantities on the basis of the linear system (12):

$$\underline{\mathbf{A}}\tilde{\mathbf{R}}_r = \tilde{\mathbf{C}}_r \quad (19)$$

To remind, within this linear system, the system matrix $\underline{\mathbf{A}}$ and the modified residual concentration profile $\tilde{\mathbf{C}}_r$ are known. However, $\tilde{\mathbf{R}}_r$ is the unknown rate profile, which has to be estimated from this system of linear equations.

This system (19) could instantly be solved for the unknown rate profile $\tilde{\mathbf{R}}_r$ by $\tilde{\mathbf{R}}_r = \underline{\mathbf{A}}^{-1}\tilde{\mathbf{C}}_r$. But as $\mathbf{F} = \underline{\mathbf{A}}^{-1}$ the resulting rate profile might also be completely wrong, as the matrix \mathbf{F} is very ill-conditioned. Although there have been a lot of mathematical calculations up to this point, we have not done anything to deal with the ill-conditionedness of this matrix $\mathbf{F} = \underline{\mathbf{A}}^{-1}$.

Here, Tikhonov regularization (see e.g. Engl et al. [2000], Björk [1996], Hofmann [1999]) comes into play. Instead of searching the rate values such that the measured concentration data are matched in the best way (which would be the solution $\tilde{\mathbf{R}}_r = \underline{\mathbf{A}}^{-1}\tilde{\mathbf{C}}_r$), a compromise is searched for. This compromise tries to fit the concentration data on the one hand, but seeks smooth and realistic rate profiles on the other hand. In mathematical terms, this compromise can be expressed by finding that rate profile $\tilde{\mathbf{R}}_r$ that minimizes the following cost function:

$$M_\alpha(\tilde{\mathbf{R}}_r) := \|\underline{\mathbf{A}}\tilde{\mathbf{R}}_r - \tilde{\mathbf{C}}_r\|_2^2 + \alpha \Omega(\tilde{\mathbf{R}}_r) = \min ! \quad (20)$$

Here, $\|\cdot\|_2$ denotes the Euclidean norm of a vector, and α is a free parameter. The first term on the right side, forces the solution to match the concentration data. However, the second term, $\alpha \Omega(\tilde{\mathbf{R}}_r)$ tries to push the solution towards rate profiles with a 'good' behavior. Here, the Tikhonov parameter α can be used to give this term more weight.

This additional cost term $\alpha \Omega(\tilde{\mathbf{R}}_r)$ can be constructed in such a way that large maxima and minima, or strong oscillations of the obtained solution $\tilde{\mathbf{R}}_r$ lead to high values of this cost function:

$$\Omega(\tilde{\mathbf{R}}_r) := \|\tilde{\mathbf{R}}_r\|_2^2 + \lambda \|\tilde{\mathbf{R}}_r'\|_2^2 + \lambda \|\tilde{\mathbf{R}}_r''\|_2^2$$

Here, λ is a second free parameter ≥ 0 , and $\tilde{\mathbf{R}}_r'$ denotes the first discrete derivative of the residual rate profile in the interval $[z_2, z_{N-2}]$, and $\tilde{\mathbf{R}}_r''$ the second discrete derivative in the interval $[z_3, z_{N-2}]$.

The characteristics of the obtained residual rate profile can be influenced by choosing the appropriate value of this weight parameter λ . If $\lambda = 0$, only large maxima and minima of the residual rate are punished. Yet, the obtained profile could still be quite noisy with a lot of fluctuations. If a smooth solution is desired, the values of λ should also be high. Therefore, the parameter λ can be considered as a kind of smoothing parameter.

Now it becomes obvious, why a constant mean net consumption and production rate has been introduced for the considered depth interval. If $\alpha > 0$ is very large, strong deviations from the mean rate are punished. This means that a very large α forces deviations from the mean rate to be zero, which finally leads to the constant mean rate profile. If this mean rate had not been introduced and the total rate profile had to be estimated instead, a very large α would result in a zero total rate profile.

After defining this cost function, it is still necessary to find a solution $\tilde{\mathbf{R}}_r$ that minimizes the cost function. To do this, it is helpful to write the additional term in a different way replacing the Euclidean norm with the scalar product $\langle \cdot, \cdot \rangle$:

$$\begin{aligned}
\Omega(\tilde{\mathbf{R}}_r) &= \|\tilde{\mathbf{R}}_r\|_2^2 + \lambda \|\tilde{\mathbf{R}}_r'\|_2^2 + \lambda \|\tilde{\mathbf{R}}_r''\|_2^2 \\
&= \langle \tilde{\mathbf{R}}_r, \tilde{\mathbf{R}}_r \rangle + \lambda \langle \underline{\mathbf{L}}_1 \tilde{\mathbf{R}}_r, \underline{\mathbf{L}}_1 \tilde{\mathbf{R}}_r \rangle + \lambda \langle \underline{\mathbf{L}}_2 \tilde{\mathbf{R}}_r, \underline{\mathbf{L}}_2 \tilde{\mathbf{R}}_r \rangle \\
&= \langle \tilde{\mathbf{R}}_r, \tilde{\mathbf{R}}_r \rangle + \lambda \langle \underline{\mathbf{L}}_1^T \underline{\mathbf{L}}_1 \tilde{\mathbf{R}}_r, \tilde{\mathbf{R}}_r \rangle + \lambda \langle \underline{\mathbf{L}}_2^T \underline{\mathbf{L}}_2 \tilde{\mathbf{R}}_r, \tilde{\mathbf{R}}_r \rangle \\
&= \langle \underline{\mathbf{B}} \tilde{\mathbf{R}}_r, \tilde{\mathbf{R}}_r \rangle \\
&\text{with } \underline{\mathbf{B}} := \mathbf{Id} + \lambda \underline{\mathbf{L}}_1^T \underline{\mathbf{L}}_1 + \lambda \underline{\mathbf{L}}_2^T \underline{\mathbf{L}}_2
\end{aligned} \tag{21}$$

Here, the new matrix $\underline{\mathbf{B}} \in \mathbb{R}^{(N-2) \times (N-2)}$ is defined with the identity matrix $\mathbf{Id} \in \mathbb{R}^{(N-2) \times (N-2)}$, and with the matrices $\underline{\mathbf{L}}_1 \in \mathbb{R}^{(N-3) \times (N-2)}$ and $\underline{\mathbf{L}}_2 \in \mathbb{R}^{(N-4) \times (N-2)}$ for the determination of the first and second derivative of the discrete rate function. These matrices are given by:

$$\underline{\mathbf{L}}_1 := \frac{1}{\Delta z} \begin{pmatrix} -1 & 1 & 0 & 0 & \cdots & 0 \\ 0 & -1 & 1 & 0 & \cdots & 0 \\ \vdots & \ddots & \ddots & \ddots & \ddots & \vdots \\ 0 & \cdots & 0 & -1 & 1 & 0 \\ 0 & \cdots & 0 & 0 & -1 & 1 \end{pmatrix} \in \mathbb{R}^{(N-3) \times (N-2)}$$

and

$$\underline{\mathbf{L}}_2 := \frac{1}{(\Delta z)^2} \begin{pmatrix} 1 & -2 & 1 & 0 & 0 & \cdots & 0 \\ 0 & 1 & -2 & 1 & 0 & \cdots & 0 \\ \vdots & \ddots & \ddots & \ddots & \ddots & \ddots & \vdots \\ 0 & \cdots & 0 & 1 & -2 & 1 & 0 \\ 0 & \cdots & 0 & 0 & 1 & -2 & 1 \end{pmatrix} \in \mathbb{R}^{(N-4) \times (N-2)}$$

Then from Hofmann [1999] and with relation (21), the minimizing residual profile can be obtained by:

$$\tilde{\mathbf{R}}_r^\alpha = (\underline{\mathbf{A}}^T \underline{\mathbf{A}} + \alpha \underline{\mathbf{B}})^{-1} \underline{\mathbf{A}}^T \tilde{\mathbf{C}}_r \tag{22}$$

Or, in a more compact form:

$$\tilde{\mathbf{R}}_r^\alpha = \underline{\mathbf{H}} \tilde{\mathbf{C}}_r \tag{23}$$

with

$$\underline{\mathbf{H}} := (\underline{\mathbf{A}}^T \underline{\mathbf{A}} + \alpha \underline{\mathbf{B}})^{-1} \underline{\mathbf{A}}^T \tag{24}$$

where $\underline{\mathbf{A}}^T$ denotes the transposed matrix of the matrix $\underline{\mathbf{A}}$. The notation $\tilde{\mathbf{R}}_r^\alpha$ denotes, that the rate profile is estimated via Tikhonov regularization and still depends on the regularization (or Tikhonov) parameter α .

A.5 Estimating the Optimal Tikhonov Parameter

The solution, obtained from Eq. (22) still depends on the choice of the smoothing parameter λ and the Tikhonov parameter α . Therefore, these parameters should be chosen in a proper way. If the parameters α and λ are too high, the obtained rate function is smooth without any very large maxima and minima, which denotes a stable behavior. On the other hand, due to the forced smoothness, the reconstructed rates may differ from the real rates in some intervals, and also the reconstructed concentration data might not be fitted correctly. If the free parameters α and λ are too small, the fitted concentration profile will be closer to the measured data, but the reconstructed rate function might show unrealistically high maxima and

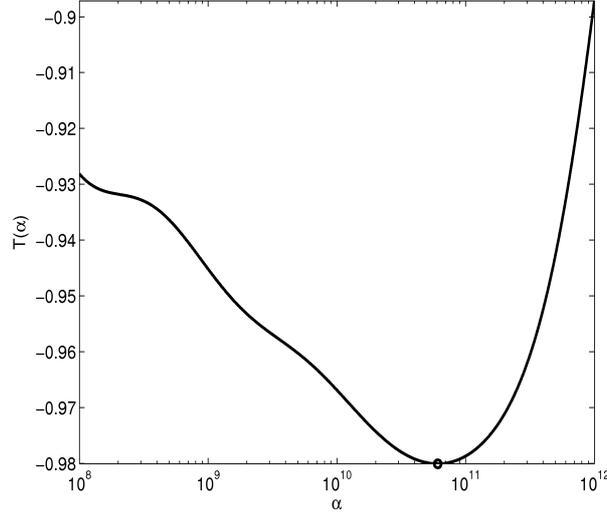


Figure 11: Example of the ratio criterion $T(\alpha)$ defined in Eq. (25) for finding an 'optimal' Tikhonov parameter α .

minima. Therefore, the parameters should be chosen properly on the basis of a reasonable criterion. Here, at least one criterion is presented for estimating the Tikhonov parameter α .

In Engl et al. [2000] and Hofmann [1999], several selection criteria for estimating an optimal α parameter (for a fixed λ parameter) are presented. Among these criteria are the famous *L-curve* criterion of P.C. Hansen and the *General Cross-Validation* criterion (Wahba [1990]). After some tests with these different criteria it was found that the so called *ratio criterion* proposed by A.N. Tikhonov is a good candidate. With this parameter selection criterion, the optimal α is chosen such that the following function $T(\alpha)$ is minimized:

$$T(\alpha) := - \frac{\|\underline{\mathbf{A}} \left(\alpha \frac{d\tilde{\mathbf{R}}_r^\alpha}{d\alpha} \right) - (\tilde{\mathbf{C}}_r^\alpha - \tilde{\mathbf{C}}_r)\|_2^2}{\|\tilde{\mathbf{C}}_r^\alpha - \tilde{\mathbf{C}}_r\|_2^2} = \min ! \quad (25)$$

with $\tilde{\mathbf{C}}_r^\alpha = \underline{\mathbf{A}}\tilde{\mathbf{R}}_r^\alpha$, and $\tilde{\mathbf{R}}_r^\alpha$ denotes the solution from Eq. (22) for given α and λ . In addition, the derivative term $\frac{d\tilde{\mathbf{R}}_r^\alpha}{d\alpha}$ is given by:

$$\frac{d\tilde{\mathbf{R}}_r^\alpha}{d\alpha} = -(\underline{\mathbf{A}}^T \underline{\mathbf{A}} + \alpha \underline{\mathbf{B}})^{-1} (\underline{\mathbf{B}}\tilde{\mathbf{R}}_r^\alpha)$$

Applying this criterion to real data, one often finds that the function $T(\alpha)$ has several local minima in a given parameter range of α . In that case, one of the larger α values is chosen to obtain a more robust estimate of the rate function. In Fig. 11, a possible graph of this $T(\alpha)$ function is illustrated. If the solution of the rate function is not smooth enough, a larger λ value could be chosen, with which a new optimal α value can be determined by criterion (25). So, the 'optimal' parameters λ and α can be chosen through an iterative procedure.

A.6 Obtaining the final solutions

Once the optimal parameters have been selected and an estimate of the residual rate profile $\tilde{\mathbf{R}}_r^\alpha$ has been obtained, the total rate profile and the total fitted concentration profile can be calculated.

At first, to obtain the total rate in reduced depth interval $[z_2, \dots, z_{N-1}]$ the estimated constant mean rate is added to the residual rate:

$$\mathbf{R}_r^\alpha = \bar{\mathbf{R}}_r + \tilde{\mathbf{R}}_r^\alpha \quad (26)$$

In order to extend the estimated rate profile to the boundary points, it is assumed, that the first derivative of the rate profile is zero close to the boundaries of the total depth interval. Therefore, the total rate on the total depth interval $[z_1, \dots, z_N]$ is obtained by:

$$\mathbf{R}^\alpha = \left(\tilde{R}_r^\alpha(z_2), \tilde{\mathbf{R}}_r^\alpha, \tilde{R}_r^\alpha(z_{N-1}) \right)^T \quad (27)$$

To this estimated rate function \mathbf{R}_α in the considered depth interval, there is a corresponding solute concentration profile \mathbf{C}^α given by the solution of the discrete form of Eq. (1). As explained in the appendix, this solution can be obtained via Eq. (28) and the imposed boundary conditions. When presenting the results of the REC numerical procedure in later sections of this manuscript, these profiles \mathbf{C}^α will be the smooth curves through the measured concentration data.

Finally, to obtain the corresponding total concentration profile from the estimated total rate profile \mathbf{R}_r^α (given in the interval $[z_2, \dots, z_{N-1}]$), based on equations (10) and (12), the following relation can be obtained:

$$\mathbf{C}_r^\alpha = \underline{\mathbf{A}}(\mathbf{R}_r^\alpha - \mathbf{d}_r) \quad (28)$$

Here, \mathbf{d}_r is build from the boundary conditions as explained before. Furthermore, in order to also get the values at the boundary points, the prescribed boundary conditions must be taken into account. With the known concentrations $\mathbf{C}_r^\alpha = (C_2^\alpha, \dots, C_{N-1}^\alpha)^T$, one obtains at the first and last grid point:

$i = 1 :$

Dirichlet : $C_1^\alpha := C_{top}$

von Neumann : $C_1^\alpha := \frac{4}{3}C_2^\alpha - \frac{1}{3}C_3^\alpha - \frac{2}{3}\Delta z m_{top}$

$i = N :$

Dirichlet : $C_N^\alpha := C_{bottom}$

von Neumann : $C_N^\alpha := \frac{4}{3}C_{N-1}^\alpha - \frac{1}{3}C_{N-2}^\alpha + \frac{2}{3}\Delta z m_{bottom}$

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