SiMBaFi
Simulation Model Bank Filtration

Calculation of predicted concentrations of pharmaceutical compounds in groundwater at bank filtration sites

Manual

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1. Objectives and Background

1.1 Overview and Purpose

The program SiMBaFi serves as a tool to calculate the predicted environmental concentrations (PEC) of pharmaceutical compounds in groundwater at bank filtration sites. Based on the predicted environmental concentration of a pharmaceutical compound in the surface water the concentration in groundwater is calculated using two kinds of information:

- Physical and chemical properties of the compound;
- Flow time between shore line and groundwater well.

The user has to enter the compound properties (Kd, DT50 and Koc), which are used afterwards to calculate transport parameters.

The flow time of groundwater at a bank filtration site is specified by four variables

1. screened interval,
2. hydraulic conductivity of the aquifer (kf),
3. extraction rate at the groundwater well and
4. distance between groundwater well and shore line (entry point of surface water).

Based on intensive research on all major German bank filtration sites values for these four variables were identified which represent all sites in Germany. A groundwater model was generated using the program code MODFLOW and groundwater flow velocities were calculated for each and every site.

Statistical analysis on groundwater flow time was performed for all data sets and three cases were chosen to represent 5, 20 and 50 percentile of observed values at German bank filtration sites (see table 1).

Table 1: Default flow times and model variables

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Case 1</th>
<th>Case 2</th>
<th>Case 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydraulic conductivity (kf) [m/s]</td>
<td>0,02</td>
<td>0,007</td>
<td>0,002</td>
</tr>
<tr>
<td>Extraction rate [m³/d]</td>
<td>3000</td>
<td>2000</td>
<td>1000</td>
</tr>
<tr>
<td>Surface water to well distance [m]</td>
<td>10</td>
<td>30</td>
<td>100</td>
</tr>
<tr>
<td>Screened interval [meter below ground level (m. bgl.)]</td>
<td>5-10</td>
<td>10-20</td>
<td>20-30</td>
</tr>
<tr>
<td>Calculated flow time [d]</td>
<td>0,15</td>
<td>5</td>
<td>110</td>
</tr>
</tbody>
</table>

However, groundwater flow time between the shore line (entry point of surface water) and the groundwater well may be entered manually, in case this information is provided.
Finally, groundwater flow time can be derived from a query of the groundwater model results in the database of SiMBaFi using values for every single of the four variables from bank filtration sites to retrieve individual groundwater flow times.

For brief information about calculation factors and methods see the manual appendix.

1.2 Calculation Routines

The calculation of the predicted environmental concentration in groundwater (PEC\textsubscript{GW}) is performed in six steps, which are described below.

1. Step: Input of $K_{oc}$

The $K_{oc}$ serves as a threshold value and an input is optional. The calculation with a $K_{oc}>10,000$ L/kg is not feasible following the EMEA guideline (EMEA, 2006), as substances with an average $K_{oc}>10,000$ L/kg are regarded immobile.

2. Step: Calculation of retardation

The retardation is calculated applying the following equation:

$$R_f = 1 + \frac{(1-n)}{n} \rho_s \cdot K_d$$

with

- $R_f$ retardation factor [-]
- $n$ porosity [-]
- $\rho_s$ solid density [g/cm\(^3\)]
- $K_d$ sorption isotherm [ml/g]

The porosity was set to a default value of 0.35 which is typical for an aquifer composed of sand and gravel. The solid density was set to a default value of 2.65 g/cm\(^3\), representing characteristic density for quartz as the main component of porous aquifer systems.

3. Step: Calculation of compound transport velocity

The retarded velocity of the compound is calculated with the following equation:

$$v_{compound} = \frac{v_{GW}}{R_f}$$

with

- $v_{compound}$ flow velocity of compound [m/d]
- $R_f$ retardation factor [-]
- $v_{GW}$ flow velocity of groundwater [m/d]

4. Step: Calculation of transport time for the compound

The transport time for the compound for the distance between shore line and production well is calculated using the equation:

$$t_{compound} = \frac{x}{v_{compound}}$$

with

- $t_{compound}$ flow time for the compound [d]
- $x$ distance between surface water and well [m]
\( v_{\text{compound}} \) flow velocity of compound [m/d]

Remark: The calculation routine of SiMBaFi combines the equation of step 3 and step 4 to:

\[
t_{\text{compound}} = t_{\text{gw}} \cdot R_f
\]

with

\( t_{\text{gw}} \) groundwater flow time

As the distance between surface water and production well is fixed no flow velocities have to be calculated.

5. Step: Calculation of elimination

The (biological) degradation of the compounds during their transport from the surface water to the production well is calculated with an exponential equation:

\[
C = C_0 \cdot e^{-\lambda t_{\text{compound}}}
\]

\( c \) concentration at production well [ng/L]
\( c_0 \) initial concentration [ng/L]
\( \lambda \) decay constant [1/d]
\( t_{\text{compound}} \) transport time for the compound [d]

with

\[
\lambda = \frac{\ln 2}{DT_{50}}
\]

\( \lambda \) decay constant [1/d]
\( DT_{50} \) disappearance time of 50 % of the compound; here used as half-life time of the compound [d]

6. Step: Dilution

The program offers the possibility of manually choosing the percentage of bank filtrate at the production well. The resulting PEC\(_{GW}\) is calculated with the equation:

\[
PEC_{GW} = c \cdot \left( \frac{bf}{100} \right)
\]

PEC\(_{GW}\) predicted environmental concentration in groundwater [ng/L]
\( c \) concentration at production well [ng/L]
\( bf \) percentage of bank filtrate in groundwater at production well [-]

2 Technical Information

2.1 Application Platform

SiMBaFi is a Microsoft Access\(^\circledast\) application. Therefore, implementation of MS Access\(^\circledast\) in the version 2002 or higher is required to run the program. The software was tested exclusively under the operating system Windows XP\(^\circledast\).
The application is delivered as an mde-file. Users are not able to read the source code or open forms and reports. Because the database window of MS Access© is hidden, it is also not possible to open database tables or queries.

2.2 Installing SiMBaFi

To install the application, simply copy the database file simbafi_version.mde, the icon simbafi.bmp and this manual to any directory of a network drive or of the computer hard disk with a free memory space of at least 75 MB. Then create a link to the file simbafi_version.mde on your desktop. To execute the program double click on the filename in a file manager (Explorer, Commander,...) or on the icon on your desktop.

It is not required to login as a computer administrator to install or run the program. It is however necessary to have writing permission for the directory which contains the application file.

3 User Interface and Functionality

Most functions, like entering and displaying data are concentrated in one main form. This main form contains buttons to start two kinds of reports and a further form to show the specifications of the software.

Starting the application will open the main form, which then moves to a new and empty dataset. If the main form is closed, the application will quit.

3.1 Main Form “Data Input and Evaluation”

3.1.1 Layout

The main form is divided into two parts with different colors. The blue area comprises all fields to enter data, the buttons to navigate between datasets and to calculate concentrations at default flow times.

The yellow and red colored section offers two optional calculation routines based on either a computed and/or a manually entered groundwater flow time.

All fields of the main form including calculation results are saved in a single database table. See section 3.1.6 for error messages.

3.1.2 Data Input

The colored fields in the main form are mandatory fields. These fields are either to identify a dataset or to run a calculation. If you decide to delete a dataset while entering data, you have to complete the mandatory fields in the header and the operation section first. Otherwise an error message pops up.

The following description of the data fields corresponds to the graphical structure of the main form.

3.1.2.1 Header

The field ID in the header part assigns a unique number to every dataset and is filled automatically.
The field *Date* allows date format only.

### 3.1.2.2 Operation

The operation component gives some general information on the pharmaceutical substance and the calculation mode. The reference number for the operation can be entered.

All fields are list boxes. A list contains any text saved in this field. It is possible either to choose a text from a list or to enter a new text. This facilitates the handling of data input, but does not provide a search function. You will not retrieve a saved dataset by selecting a list item.

In addition to the fields *Pharmaceutical compound* and *Brand name* the input of a *Calculation mode* offers the possibility to calculate several concentrations of the same compound.

### 3.1.2.3 Input Data (compound data)

The data input to calculate the predicted groundwater concentration (see section 1.2) is performed in the section shown below.

The value entered in the field $K_{oc}$ serves as a threshold. In case of a $K_{oc} > 10,000$ mL/g no further calculations will be performed as the substance is regarded as not mobile and a message will pop up. The default value of the *Percentage of bank filtrate* is set to 100%, but all percentages between 50% and 100% will be accepted.

### 3.1.2.4 Additional Information

In this part an additional comment as well as the names of the author and the responsible institution may be inserted.
3.1.3 Calculation at Default Flow Times

After completion of the mandatory fields the concentration of a pharmaceutical substance at default groundwater flow times of 0.15, 5 and 110 days is computed by clicking the button *Calculate*, which is shown in the screenshot below.

The calculation will be carried out and the computed values are saved in the database and displayed in the main form. In case of an error message see section 3.1.6.

3.1.4 Button Bar

Button with darker blue background navigate and operate some further functions as a data backup.

The buttons are explained from left to right on the bar.

- A click on this button deletes all (standard and user-defined) calculation results of the open dataset.

- This button activates the search function of MS Access. Before starting this button, it is advised to click in the field with the searched item. Pressing the search button will then open a dialog box.

  In the first list box the text or number to be searched for is entered. The field below shows the name of the field in the main form, which actually has the focus. Search takes place only in this field.

  When using the replacement function it is important to notice, that after substituting a value the main form will automatically show the next dataset, in which the searched value is detected.

- The buttons in the bar showing arrows enable the user to navigate between the datasets in the following sequence:
  - first dataset
  - previous dataset
  - next dataset
  - last dataset
  - delete active dataset
To enter a new dataset press the button labeled *Add new operation*.

This button opens the report window showing the entered and the computed data at default flow times (see section 3.2).

A click on this button will close the application after opening a dialog box with the request for a confirmation to quit. It may take a short time to exit SiMBaFi, because a routine to compress the database size is activated.

### 3.1.5 Extended Calculation Options

The calculation of pharmaceutical concentrations at variable flow times is carried out in the yellow colored area of the main form.

After a click on the button *New user-defined calculation* one further button in each one of the both red sectors will appear.

While moving between datasets only the fields with attached values will be visible. All other fields will be activated when data is inserted.

#### 3.1.5.1 Calculation with manual Flow Time Input

A click on the button *Calculation using a manual flow time* in the upper red area, will activate an input box to enter a flow time of free choice. Activating the button *Calculate* on the right side opens another field displaying the computed concentration at the entered flow time. If the flow time field is already visible, the value can be changed and the calculation is carried out by clicking on the *Calculate* button again. If the values of flow time and concentration are cleared by the *Delete result* button, a new calculation has to be started by activating the button *Calculation using a manual flow time input* again.

#### 3.1.5.2 Calculation with queried Flow Time

The calculation option in the lower red segment applies the results of groundwater modeling, which are queried from a table in the database. After pressing the button *Calculation using a queried flow time* four list boxes, which are numbered from left to right, will appear. The selectable entries in the list boxes derive from the above mentioned table, which does not contain flow time calculations for every combination of the four variables. Therefore the second list will show only those groundwater extraction rates, for which the table contains a calculation result in combination with the chosen depth of the screened interval. The
selection from the four list boxes must be proceeded from left to right (1. to 4.). Otherwise the list constraints are not applying and an error message may appear.

Pressing the Calculate button will open two fields, displaying the result of the flow time query and the corresponding calculated concentration. The Delete button operates in the same way as described in section 3.1.5.1.

### 3.1.6 Data Exchange

The data exchange section is relevant in terms of data security.

#### Table 2: Exported Table Columns

<table>
<thead>
<tr>
<th>Exported Columns</th>
<th>ID</th>
<th>Reference number</th>
<th>Compound</th>
<th>Brand name</th>
<th>Calculation Mode</th>
<th>PECSW</th>
<th>KOC</th>
<th>Kd</th>
<th>DT50</th>
<th>Percentage bank filtrate</th>
<th>PECGW 0.15 d</th>
<th>PECGW 5 d</th>
<th>PECGW 110 d</th>
<th>Flow time manual</th>
<th>PECGW manual</th>
<th>Flow time query</th>
<th>PECGW query</th>
<th>Screened interval</th>
<th>Extraction rate</th>
<th>kf</th>
<th>Well bank dist</th>
<th>Comment</th>
<th>Author</th>
<th>Institution</th>
<th>Date</th>
</tr>
</thead>
</table>

The Export all data button carry the saved database table in an external data file with the columns shown in table 2.

Users are advised to run this backup function regularly. Otherwise in case of file corruption all data are lost. After pressing the export button it is requested to choose a file format, a file name and a directory. For example, in Excel sheets up to 65,000 data sets can be stored.

To restore a former data inventory a previously exported table in format MS Excel must be saved under the name and the path c:\SiMBaFI\dataimp.xls. After pressing the button Restore data inventory a user is prompted to confirm the replacement of all data in the program SIMBAFI through the data from the external Excel file. It has to be emphasized, that all existing data in SIMBAFI will be deleted. For actualization reasons the application will close automatically after finishing the import routine. The imported data will be available with restarting the database.

### 3.1.7 Routines to check Data Integrity

Messages of the programmed routines are displayed in English language, whereas all messages activated by MS Access will appear in the language of the MS Access implementation. An error message of MS Access will for example be activated at any violation of field format restrictions (number, date, ..). An English error message appears in case of entering negative values in the numerical fields of compound properties.

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If data in the sections header, operation and compound data of a saved dataset will be changed, the user is asked to confirm the deletion of all calculation results. This routine applies to the field $K_{oc}$ only in case of an input value above 10,000 mL/g. Furthermore a $K_{oc}$ value exceeding 10,000 mL/g will disable any calculation displaying a message box, that there is no compound transport under this condition.

If an invalid combination of values to query the flow time resulting from the groundwater modeling is chosen an error message will demand a change of data input.

Several routines of data actualization make sure, that entered data will be saved with operating any of the program functions (open report, new calculation, quit,…).

### 3.2 Reports

There are two report versions, which both represent the actual main form dataset. The standard report shows the concentrations at default flow times, whereas the extended report also includes user-defined calculation results. A report showing the present dataset in the main form is opened by pressing the button *Report with standard calculation* in the navigation bar or activating the button *Report including user-defined calculations*. The report design reflects the main form structure. Users are not able to change the general layout of both reports. But there is the possibility to export a report to a file and then modify the contents.

To print or export a report, first open it and then click with the right mouse button on the report. The appearing window provides an export and a print function as an MS Access standard. A standard report will only open, if concentrations at default flow times are computed. An extended report can be started after accomplishing at least one user defined calculation.

### 3.3 Software Information and Manual

On the right side of the main form header are two buttons. The *Info* button will open a window informing about number and publishing date of the executed application version as well as about participating and funding persons/institutions and the assigned project.

The *Manual* button will open the provided pdf-file of the manual. It has to be saved in the same directory as the file with the application database (e.g. SiMBaFi_V109.mde).

Otherwise the manual will not open using the *Manual* button.

The manual front page shows a screenshot of the Info form indicating the program version this manual refers to.

### 4 License

The distribution of this software is organized by the German UMWELTBUNDESAMT, which may charge a protection fee.

In case of any requests information is given also by HYDOR CONSULT GMBH, Berlin or the TECHNISCHE UNIVERSITAET BERLIN, DEPARTMENT OF APPLIED GEOSCIENCES, HYDROGEOLOGY GROUP.
5 Appendix

The program SiMBAFi includes three different possibilities of flow time input for calculation of the $P_{EC_{Groundwater}}$ ($P_{EC_{GW}}$). The standard application is based on three default flow times for groundwater flow from the surface water to the production well. These three groundwater flow times are 0.15, 5 and 110 days, representing the 5, 20 and 50 percentile of observed values at German bank filtration sites. All three default flow times are the result of a groundwater model approach and subsequent statistical evaluation of the modeling results.

The extended application includes the possibility of manually entering a residence time for groundwater flow from the surface water to the production well.

The third possibility is manually entering the parameter: screen interval, extraction rate, hydraulic conductivity ($k_i$) and distance between surface water and production well. Based on the results of the groundwater flow modeling a flow time for the specific case is displayed. Some combinations have resulted in falling dry of the well and are therefore not displayed. All combinations which produce unrealistic results are omitted.

The following figure shows a generalized schematic of a river bank filtration system.

![Figure 1: Schematic cross section of a river bank filtration system. The production well pumps groundwater from the aquifer which infiltrates from the surface water.](image)

In addition to the flow time the user must enter a value for the sorption coefficient ($K_{d}$) and the disappearance time ($DT_{50}$). The input of $K_{oc}$ is optional. With a $K_{oc} > 10,000$ L/kg a calculation of $P_{EC_{GW}}$ is not possible following the EMEA guideline, that substances with an average $K_{oc} > 10,000$ L/kg are regarded immobile (EMEA, 2006).

The determination of $K_{d}$, $K_{oc}$ and $DT_{50}$ is described in several OECD guidelines. The tests are performed under different laboratory conditions. The following parameters are significant factors for the laboratory tests: pH value, redox potential, temperature, sediment texture and natural organic matter content of the sediment. They have an important influence on the sorption and degradation behavior of the pharmaceutical compounds in groundwater. In the
following sections, the range of these parameters in groundwater is discussed and typical values for four German bank filtration sites are presented in table 3.

In general all laboratory tests for determination of sorption and/or degradation data should be performed under (water)saturated conditions in a water/sediment system which is in good accordance with aquifer conditions. The quality of data available for model input has a significant effect on the quality of the calculation result. For sorption coefficients and degradation rates correction factors for e.g. temperature can be applied.

**pH value**
The pH values in natural groundwater normally range between 5.5 and 8.0 (HÖLTING, 2009). In general groundwater originating from silicatic rock has a lower pH value than water from limestone aquifer. Exceptions are acid mine drainages with pH <5 and carbonate-rich groundwater with pH values >8 (MATTHEß, 1990). At bank filtration site pH values between 6.5 and 9.5 can be expected (TRINKWASSERVERORDNUNG, 2001). The pH values at four German bank filtration sites vary between 6.5 and 7.8 in a neutral range (see Table 3).

**Aquifer material/ soil texture (clay content, natural organic matter (NOM) content)**
The texture of an unconsolidated porous aquifer at bank filtration sites is in general sand and gravel with a varying content of silt and clay. The texture mostly depends on the deposition conditions, which can be marine, alluvial, fluvial, lacustrine or glacial. Furthermore the texture of the source material is important for the resulting aquifer composition (MATTHEß, 1990). Most bank filtration sites are located in alluvial aquifer systems along riverbanks. These aquifers consist of sediments ranging from sand, to sand and gravel, to large cobble and boulders (RAY ET AL. (EDS.), 2002).

The sorption capacity of aquifer material depends on the fraction of organic carbon in the sediment. Sorbents with a TOC content of < 0.1 % ($c_{org} < 0.001$ g/g) show a low sorption. The sorption in these sediments is defined by the specific surface and the texture of the minerals (SCHWARZENBACH & GIGER, 1985, MATTHEß, 1990). The organic carbon content at the four sample sites varies between 0 and 3.46 %.

**Redox conditions**
Within the aquifer the redox conditions can range between aerobic and anaerobic conditions. Aerobic conditions represent an oxygen influenced environment. Under anaerobic conditions no free or bounded oxygen is available for degradation and transformation processes (APPELO & POSTMA, 2005). At relatively short groundwater flow times of up to 10 days aerobic aquifer conditions can be expected at bank filtrations site since oxygen-rich surface
water infiltrates and reaches after a short transport time the production well. After such short residence times the oxygen dissolved in groundwater is not yet depleted.

Applying longer flow times for the $\text{PEC}_{\text{GW}}$ calculation the oxygen in groundwater will be depleted by redox processes.

The degradation rates depend on the redox conditions occurring within the aquifer. Generally, for most compounds biodegradation under aerobic conditions is faster than biodegradation under anaerobic conditions (MATTHEß, 1990; LANGGUTH & VOIGT, 2004). This is also true for most pharmaceuticals for human medical care.

Groundwater temperature

The temperature of groundwater depends on the temperature of the infiltrating surface water. At low residence times and high infiltrating rates of surface water the temperature of the infiltrating water remains mostly unchanged. The infiltrating water has a strong effect on the groundwater temperature by decreasing and/or increasing it. Therefore at bank filtration sites the groundwater strongly reflects the temperature conditions of the infiltrating surface water (MATTHEß, 1990). The groundwater temperature at the four sample bank filtration sites ranges between 8.0 and 14.2°C.

The following table lists the discussed conditions at four German bank filtrations sites as examples.

Tab. 3: Characteristics of four German bank filtration sites

<table>
<thead>
<tr>
<th>Aquifer material/ soil texture (clay content)</th>
<th>Berlin – Tegeler See</th>
<th>Berlin - Wannsee</th>
<th>Flehe - Rhine</th>
<th>Torgau/Ost – Elbe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural organic matter content sediment</td>
<td>Organic carbon content 0.0-2.1 % (MASSMANN ET AL. 2007)</td>
<td>0.2-10 % (Massmann et al. 2008)</td>
<td>Total carbon content (TOC) ranges between 0.02 and 3.46 % (ECKERT, unpublished)</td>
<td>TOC ranges between 0.013 and 0.024 %; 100 - 200 mg/kg TOC aquifer material fraction &lt; 2 mm (GRISCHEK, 2003)</td>
</tr>
<tr>
<td>Fine to coarse grained middle sand</td>
<td>Fine to coarse grained middle sand</td>
<td>Sandy gravel (ECKERT &amp; IRMSCHER, 2004)</td>
<td>Fine gravel to middle sand (GRISCHEK, 2003);</td>
<td></td>
</tr>
<tr>
<td>-----------------</td>
<td>------------------------</td>
<td>------------------------------------------------------</td>
<td>---------------------------------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td><strong>groundwater</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>10.7 (mean value, NASRI, unpublished)</td>
<td>11.1 (mean value, NASRI, unpublished.)</td>
<td>13.3 – 14.2 (ECKERT, unpublished)</td>
<td>8.0 – 12.0 (GRISCHEK, 2003)</td>
</tr>
<tr>
<td><strong>groundwater [°C]</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

K₄ and DT₅₀ values derived from laboratory tests following OECD guidelines are difficult to apply to real bank filtration sites. However, if the laboratory tests for K₄ and DT₅₀ are performed under conditions as similar as possible to the natural aquifer system conditions these values come quite near to the natural system.

Only very few DT₅₀ and K₄ values for pharmaceutical substances from literature are determined in a water/sediment-system. In many cases the DT₅₀ value was determined for surface water. These values are not suitable for groundwater since photo degradation can be an important degradation process in surface water but not in groundwater. Furthermore the determination of the K₄ value in sewage sludge is not very well applicable for the calculation of retardation within an aquifer system. Sewage sludge shows a far higher TOC content than natural sediments.

Typical aquifer conditions are summarized and should be applied in the laboratory tests to study the behavior in groundwater at a bank filtration site:

- pH value water: 6.5 – 9.5;
- sediment material: sand to gravel with low TOC, silt and clay content;
- redox conditions: aerobic and anaerobic conditions;
- water temperature: 10 – 15°C.