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**MODELLING CONCEPTS
AND DECISION SUPPORT
IN ENVIRONMENTAL SYSTEMS**

Editors:

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Olgierd Hryniewicz**

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The purpose of the present publication is to popularize information tools and applications of informatics in environmental engineering and environment protection that have been investigated and developed in Poland and Germany for the last few years. The papers published in this book were presented during the workshop organized by the Leibniz-Institute of Freshwater Ecology and Inland Fisheries in Berlin in February 2006. The problems described in the papers concern the mathematical modeling, development and application of computer aided decision making systems in such environmental areas as groundwater and soils, rivers and lakes, water management and regional pollution. The editors of the book hope that it will support the closer research cooperation between Poland and Germany and when this intend succeeds then also next publications of the similar kind will be published.

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CHAPTER 1

Groundwater / Soil



INVERSE MODELLING TOOL VISUAL CXTFIT FOR ONE-DIMENSIONAL TRANSPORT, SORPTION AND DEGRADATION PROCESSES DURING BANK FILTRATION

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Abstract: Successful predictions of the fate and transport of solutes during bank filtration and artificial groundwater recharge hinges on the availability of accurate transport parameters. We expand the CXTFIT code in order to improve the handling with the help of pre- and post processing modules coupled with Microsoft Excel. Inverse modelling results of column experiments with tracers, pharmaceutical residuals and algae toxins demonstrate the applicability of the advanced simulation tool. Different kind of field, semi-technical and column experiments were carried out with tracers (Bromide, Gadolinium, and Uranin), pharmaceutical residuals (e.g. Primidone, Carbamazepine) and blue algae toxins (Microcystin). First of all the model was used to estimate best fits for the transport parameters velocity v/n_c and dispersion length $\alpha_L=D/v$ regarding different types of input functions. Especially for field experiments these parameters are used as first approximations to be improved with the help of numerical modeling. For column experiments, based on these analyses inverse modeling of retardation and decay lead to a better understanding of sorption/desorption and biodegradation effects, sometimes coupled with mobile-immobile transport behavior. Results of Visual CXTFIT modeling often are used further for reactive transport simulation.

Keywords: bank filtration, advection-dispersion equation, analytical solution, inverse modelling, graphical user interface, sorption, degradation.

1. Introduction

Within the interdisciplinary NASRI research project (Natural and Artificial Systems for Recharge and Infiltration) dealing with bank filtration and artificial groundwater recharge processes, a set of column and field experiments were carried out to understand mechanisms of transport, sorption and biodegradation of different compounds. To identify these parameters in a first step an inverse modelling tool has been selected and embedded in a pre- and postprocessing routine programmed with Visual Basic for applications. This was performed using Visual CXTFIT, which is

a graphical user interface (GUI) for the CXTFIT code for parameter estimation. CXTFIT was developed at the U.S. Salinity Laboratories (Toride et al., 1995) and is based on analytical solutions of the 1D transport equation. Analytical solutions have the advantage that direct solutions of the differential equation have no problems with discretization errors, as they appear in numerical solutions. On the other hand analytical solutions exist only for specific conditions and can not be given for general boundary and initial conditions. However for the given experimental set-up in the enclosures as well as in the columns it was possible to use CXTFIT.

With the help of a graphical interface and using EXCEL worksheets and graphs, experimental data sets can easily be transferred and results – observed and fitted breakthrough curves – are depicted simultaneously. Thus, particularly experimentally working groups are enabled to handle this user-friendly simulation tool both for analysing and planning of experiments. A detailed description as well as application examples are given by Grützmacher et al. (2005), Nützmann et al. (2005) and Heberer et al. (2004). An additional step was performed using a newly developed tool for parameter inversion, written as a m-file module in MATLAB® (2002). The module has been used for inversions of transport processes only, but could be used for other applications as well. The MATLAB® module works also for the inversion of temperature time series. For such an application the module is described in detail by Holzbecher (2005) and not shown in this paper.

2. Material and Methods

2.1 Direct and inverse solution of transport model

The transport code CXTFIT 2.1 (Toride et al., 1995) utilises analytical solutions for transport parameter estimation. Solutions of the one-dimensional transport equation for the fluid phase concentration c :

$$R \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} - \mu c + \gamma, \quad (1)$$

where v is the average pore water velocity q/n_e , R is the retardation factor given by

$$R = 1 + \frac{\rho_b K_d}{n_e}, \quad (2)$$

D is the dispersion coefficient and μ and γ are combined first- and second-order rate degradation coefficients. Equation (2) denotes that solute adsorption by the solid phase is described by a linear isotherm as

$$s = K_d c, \quad (3)$$

where K_d is an empirical distribution constant. Equation (1) can be rewritten in a reduced form with dimensionless parameters as

$$R \frac{\partial C_r}{\partial t} = \frac{1}{P} \frac{\partial^2 C_r}{\partial Z^2} - \frac{\partial C_r}{\partial Z} - \mu^E C_r + \gamma^E(Z), \quad (4)$$

where C_r is the reduced volume-averaged solute concentration, P is the Peclet number, μ^E is a first-order decay coefficient ($= L\mu/v$), γ^E is a zero-order production coefficient for equilibrium transport ($= L\gamma/vc_0$), and Z and T are the dimensionless space and time variables, respectively. Solutions of (4) are presented in terms of the above dimensionless parameters, but dimensional solutions can be easily obtained by substituting the parameters back.

Analytical solutions of (4) are included in CXTFIT 2.1 for different initial and boundary conditions. Both boundary and initial conditions are optional: the Dirac delta input, multiple pulse input (with constant concentration as special case), and exponential input. Alternatively the transport equation can be taken in stochastic form and the concentrations in flux-averaged form. The non-equilibrium sorption situation can also be treated as a generalisation of equation (4).

The implemented analytical solutions are extensions of the classical solution of the advection-diffusion equation of Ogata & Banks (1961), some of which were also presented by van Genuchten (1981). Analytical solutions have the advantage that the accuracy of the results does not depend on certain numerical conditions to be fulfilled. In contrast the accuracy of numerical solutions is coupled to stability conditions as the grid-Péclet condition, the Courant- or the Neumann condition. The user of CXTFIT 2.1 thus does not have to keep an eye on such criteria for temporal or spatial step size.

CXTFIT 2.1 estimates unknown parameters using a nonlinear least-squares optimization routine based on the Levenberg-Marquardt method (Press et al. 1992). The inverse problem is solved by fitting an appropriate mathematical solution to observed solute concentration data. The model parameters are determined by minimizing an objective function defined as

$$SSQ(b) = \sum_{i=1}^N [c(x_i) - f(x_i; b)]^2, \quad (5)$$

where b represents the vector of unknowns containing M adjustable parameters b_j ($j = 1, \dots, M$), and c and f are the observed and calculated concentrations for the i th data point as obtained with the independent variable(s) x_i ($i = 1, \dots, N$). When a model depends nonlinearly on a set of M unknown parameters b_j , minimization of (5) has to be carried out iteratively (Nützmann *et al.* 1998). The derivatives of the fitted concentrations with respect to parameter b_j are evaluated by

$$\frac{\partial f(x_i; b)}{\partial b_j} \cong \frac{f(x_i; b_1, \dots, (1 + \Delta)b_j, \dots, b_M) - f(x_i; b_1, \dots, b_j, \dots, b_M)}{\Delta b_j} \quad (6)$$

The current setting for Δ is 0.01 for all parameters, but when b_j is very small or insensitive to changes in the fitted concentration, however, approximation (6) for the derivative may become inaccurate. As typical for nonlinear problems, the iteration procedure sometimes converges to different local minima depending upon the initial. Therefore, it is essential to provide realistic initial estimates of the parameters, as close to the global minimum as possible. Furthermore, CXTFIT 2.1 allows the use of maximum and minimum constraints on fitted parameters. When the new parameter value exceeds a specific maximum or minimum value due the iteration process, the value for the constraint is used for the next trial.

2.2 User interface

Visual CXTFIT is implemented in Visual Basic for use in Microsoft EXCEL. The implementation work was performed at the IGB Berlin. The program is started either by double click directly on the EXCEL file *VCxftfit.xls* or from EXCEL directly using an Add-In. At the right of EXCEL's menu bar at the top of the screen the item "Visual Cxtfit" appears, as shown in Fig. 1.

Fig. 1 depicts the new Excel menu bar after opening the worksheet. The item 'Visual Cxtfit' runs the program, the item "Options" opens a window, where path and file settings can be entered. The visual CXTFIT main window opens after selection of the 'Visual Cxtfit' menu, and it is shown in Fig. 2.



Figure 1. Appearance of CXTFIT in EXCEL.

In the main window all operational commands are gathered, like 'open', 'save', 'save as', 'new', 'exit'. The 'run' button starts the CXTFIT 2.1 code in the background and presents the results in EXCEL and ASCII-formats. In addition major options can be set in the main window: the type of the differential equation and of the concentration, if independent variables are dimensionless or not, or if the direct problem is solved only.

Within the CXTFIT 2.1 code these options are gathered in Block A, which appears in the GUI view in Fig. 2 as a footer name at the bottom. Concerning further input data the block-structure of the CXTFIT 2.1 code is represented in the user interface. In Block B various inverse modelling parameters can be specified (in Fig. 2 this block is deactivated, because the direct problem option is selected).

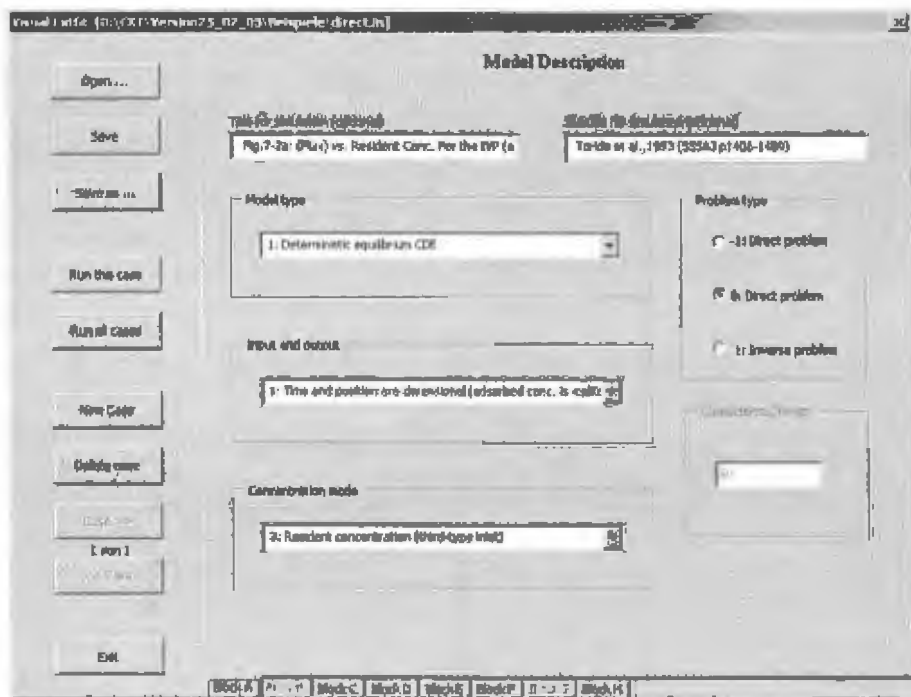


Figure 2. User Interface of visual CXTFIT.

In Block C transport parameters are set, which the program fits during an inverse modelling run, if the parameter is to be determined, or remain unchanged otherwise. Parameters selected for estimation should be given minimum and maximum constraints. In Block D the boundary conditions are set, in Block E the initial conditions. Block F deals with the production term, Block G with observed data for the inverse problem. Finally in Block H temporal and/or spatial increments for the output of the estimated analytical solution are specified by the user.

The CXTFIT 2.1 program starts after a click on the 'run'-button (see Fig. 2). There is an option to treat several cases in one run. After the run a report is given on an ASCII file, as well as tabular and graphical output in EXCEL. Examples are shown in the next sub-chapter.

3. Applications

Different kind of field, semi-technical and column experiments in the NASRI research project were carried out with tracers (e.g. Bromide, Gadolinium), pharmaceutical residuals (e.g. Primidone, Carbamazepine) and blue algae toxins (Microcystin). First of all the model was used to estimate best fits for the transport parameters velocity v/n_e and dispersion length $\alpha_L = D/v$ regarding different types of input functions. Especially for field experiments these parameters are used as first ap-

proximations to be improved with the help of numerical modeling. For column experiments, based on these analyses inverse modeling of retardation and decay leads to a better understanding of sorption/desorption and biodegradation effects, sometimes coupled with mobile-immobile transport behavior. Results of Visual CXTFIT modeling often are used further for reactive transport simulation. Three examples are given in the following sub-chapters.

3.1 Dual field-scale tracer experiment

The aim of this study is to identify the spatial distribution of the hydraulic conductivity and dispersivity of an artificial semi-technical experimental site, where bank filtration can be modelled in a combined surface water – groundwater system (Nützmann *et al.* 2004). The shallow aquifer is 3 – 4 m thick and consists of two layers of coarse and fine gravel sediments. A dual tracer experiment with Bromide (NaBr) and Gadolinium (Gd-DTPA) was carried out and the breakthrough curves (BTC's) observed at 15 groundwater observation wells with different filter depth in two transects over a travel distance of 32 m enabled a three-step analysis comprising (i) estimation of non-steady tracer input function, (ii) inverse modelling of one-dimensional groundwater transport with Visual CXTFIT and, (iii) modelling of fully 3-D flow and transport in the aquifer. Here, only results of the second step are reported.

Because of very similar boundary conditions at the shore line, the shapes of both tracer breakthrough curves differ very slightly. In Fig. 3 the temporal distribution of observed and simulated Gd-DTPA concentrations for three single wells with increased distance from the injection location can be seen.

Fig. 3A and 3B show a close agreement between measured and modelled BTC's but with slightly different values of flow velocities and dispersion. From Fig. 3C an additional mechanism like mixing of water bodies with different concentrations as a result of 3-D flow structures is detectable, what leads to a non sufficient approximation. With the help of the one-dimensional simulator Visual CXTFIT a likely range of variation for the flow velocities of the sandy and gravel layer could be identified (from 0.3 to 7.1 m per day). Again, the variation of the dispersion lengths is in a higher range than the variation of the velocities. The identified parameters demonstrate a first approximation of the spatial distribution of transport coefficients, which could be improved only by using a fully three-dimensional modelling approach.

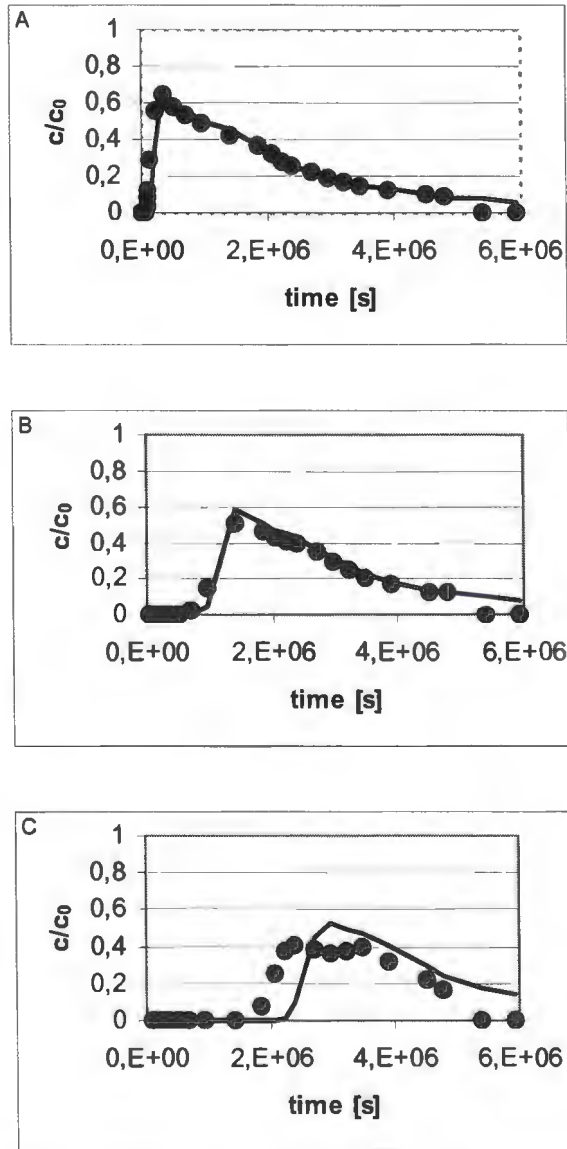


Figure 3. Measured (dots) and simulated (line) Gd-breakthrough curves (A: 2m, B: 10m, C: 22m distance from the tracer injection).

3.2 Fate of PhAC's during enclosure experiments

Several experiments were carried out with so-called enclosures (cylindrical pipes with about 1 m height and an area of 1 m²) to study the fate of selected pharmaceuticals in a sandy soil without and with a thin clogging layer. In Figure 4 the

cross section of the enclosure is schematically depicted showing the geometry and location of sampling points.

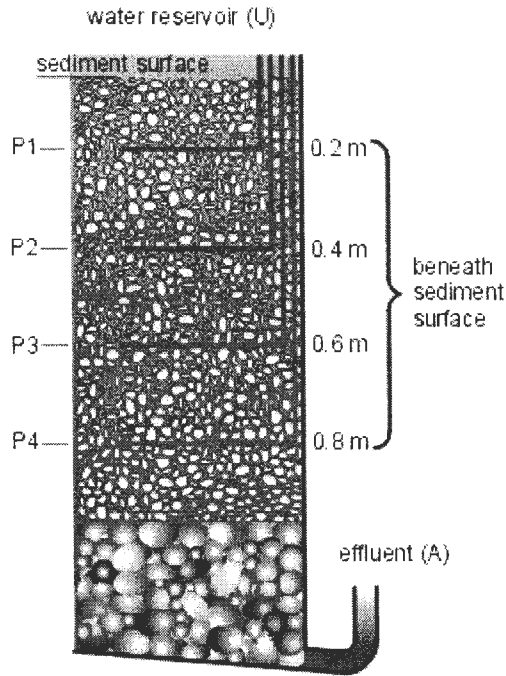


Figure 4. Cross section of enclosure.

Five pharmaceuticals, namely clofibric acid, ibuprofen, primidone, carbamazepine and diclofenac were chosen for this study. All substances have already been found in the aquatic environment and have been selected as model substances due to their physico-chemical properties and their expected or reported different behaviour during groundwater recharge. Apart from their initial concentrations the observed change of concentration was quite similar for all four compounds, but the identified degradation coefficients are unequal (Tab. 1). Whereas all pharmaceuticals are retarded ($1.2 < R < 2.9$), only ibuprofen was efficiently degraded during slow sand filtration. This may indicate that ibuprofen is subject to a microbial degradation and the removal is not only a result of an adsorption to the sediment (Heberer *et al.* 2004).

Table 1. Estimated values of the decay coefficient μ [1/h] for different PhAC compounds during enclosure filtration experiments (from Mechlinski et al., 2005)

Depth below surface [cm]	Clofibric acid	Ibuprofen	Primidone	Carbamazepine	Diclofenac
40	0.0	1.6	0.0	0.0	0.09
80	0.05	2.0	0.0	0.04	0.1
40 *	0.0	2.0	0.0	0.0	0.0
80 *	0.0	2.0	0.0	0.0	0.03

(* Experiments with a clogging layer)

3.3 Transport and degradation of cyanobacterial toxins

Laboratory and technical scale experiments have also shown, that breakthrough of particle-bound as well as extracellular cyanotoxins is possible (Bricelj & Sedmak, 2001; Chorus et al., 2004). Similar to the PhAC experiments discussed above enclosure experiments are carried out to identify transport parameters like dispersion, adsorption and decay of microcystins (MCYST).

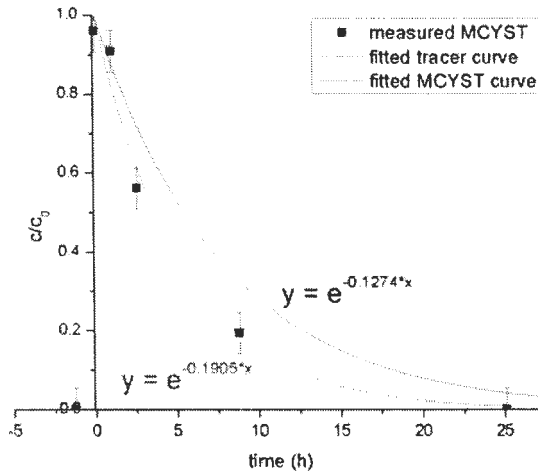


Figure 5. Measured MCYST concentration in the water reservoir, fitted decay function and fitted tracer curve during experiment E 2.

Pulse-type injection of tracer and MCVYST into the water column above the sediment layer leads to a decrease of concentration of both substances due to mixing with fresh water.

First, the normalized input concentration was estimated as a function of time as shown in Figure 5 for a tracer and MCVYST. These normalized input functions could be described for all experiments in form of an exponential curve

$$\frac{c}{c_0} = e^{-at} \quad (7)$$

where c/c_0 is the normalized input concentration, a the variable coefficient to be fitted, and t the time. For different enclosure experiments different values of a are found, detecting the mechanisms of mixing and additional biodegradation or decay. This can be explained by the higher a -value for the MCVYST function compared to the tracer ones, see Fig. 5.

Then, the BTC's of tracer and MCVYST at 4 different sampling points (20, 40, 60, 80cm depth) and the outlet (120 cm depth) of the enclosures are modeled with VisualCXTFIT using the fitted input function. From tracer BTC's the velocity v_a and dispersivity αL was estimated, whereas the retardation coefficient R and degradation rate μ was determined from MCVYST breakthroughs. The results are shown in Fig. 6 for all sampling points of one selected enclosure experiment (Grützmacher et al., 2005).

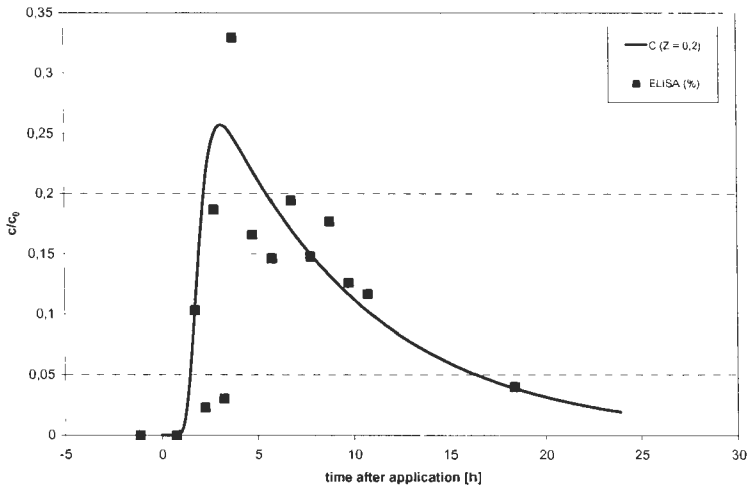


Figure 6a. Measured and modeled MCVYST breakthrough curves at 20 cm below the reservoir ($v_a = 0.17$ m/h; $D = 0.0015$ m²/h; $R = 1.8$; $\mu = 1.0$ 1/h).

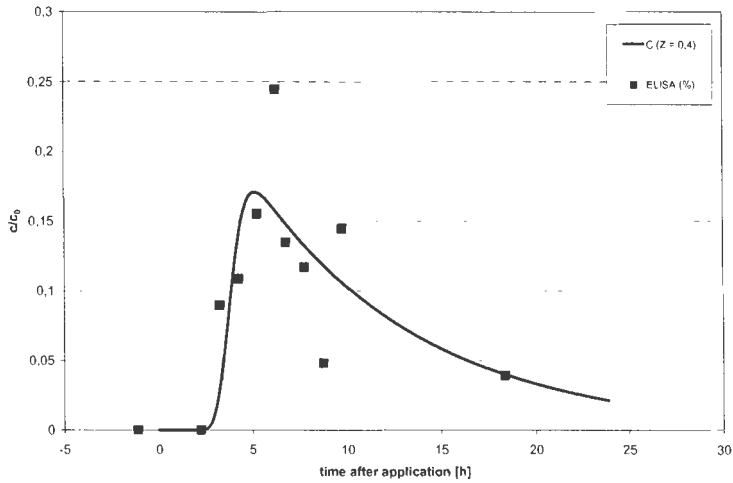


Figure 6b. Measured and modeled MCYST breakthrough curves at 40 cm below the reservoir ($v_a = 0.15$ m/h; $D = 0.0008$ m²/h; $R = 1.3$; $\mu = 0.6$ 1/h).

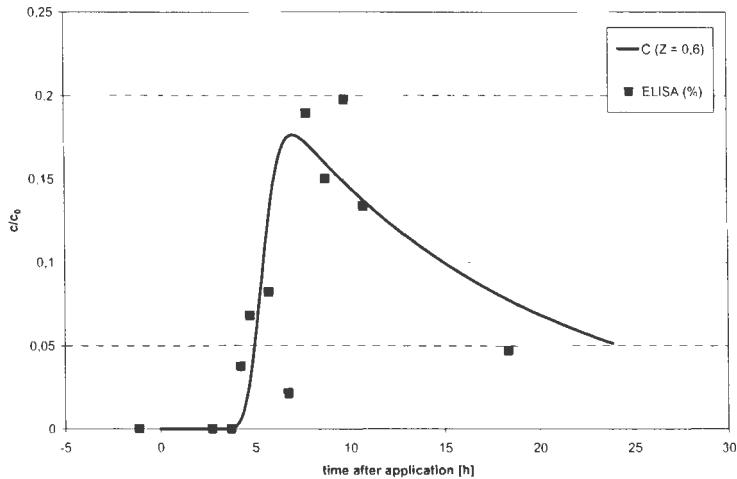


Figure 6c. Measured and modeled MCYST breakthrough curves at 60 cm below the reservoir ($v_a = 0.15$ m/h; $D = 0.0008$ m²/h; $R = 1.4$; $\mu = 0.4$ 1/h).

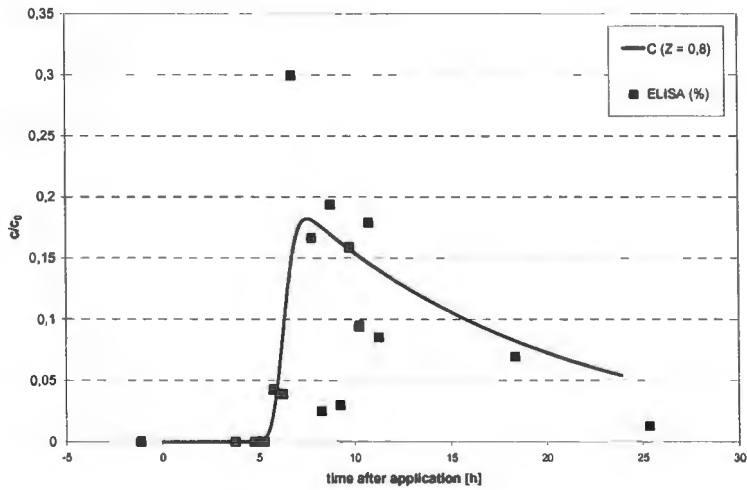


Figure 6d. Measured and modeled MCYST breakthrough curves at 80 cm below the reservoir ($v_a = 0.15$ m/h; $D = 0.0004$ m²/h; $R = 1.2$; $\mu = 0.3$ 1/h).

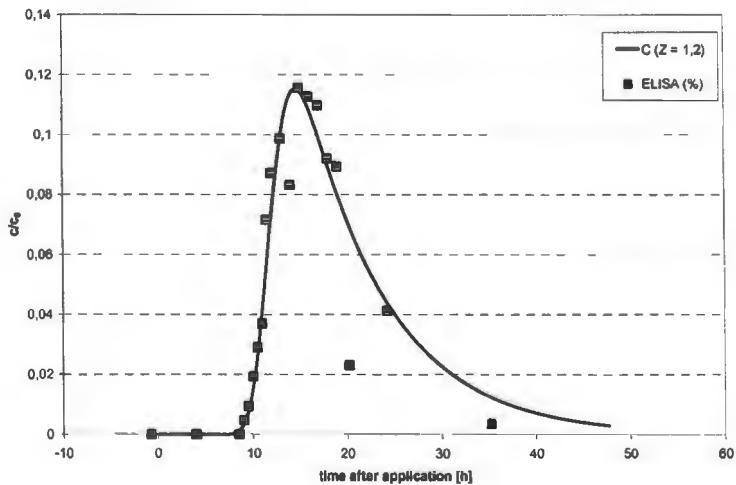


Figure 6e: Measured and modeled MCYST breakthrough curves at 120 cm below the reservoir ($v_a = 0.115$ m/h; $D = 0.0015$ m²/h; $R = 1.2$; $\mu = 0.17$ 1/h).

The identified values of retardation varies from $1.2 < R < 1.8$, whereas their distribution is not correlated with the depth. In contrast to that, the decay coefficient range from $\mu = 1.0$ [1/h] at 20 cm to $\mu = 0.17$ [1/h] at the outlet showing a decrease of microbial activity with increasing depth and a partial removal of MCYST during slow sand filtration under saturated conditions. Recent infiltration experiments during the NASRI project confirm, that MCYST breakthrough can occur at different depths depending on the biological activity at the infiltration surface, pore water flow velocity, geochemical composition of the sediments and prevailing redox conditions during infiltration.

4. Conclusions

Using the Visual CXTFIT add-in measured breakthrough curves for tracers, pharmaceuticals and algae toxins were successfully reproduced. Especially for column and enclosure experiments mechanistic studies are carried out to find basic transport parameters. Even in the case of more complex flow situations during field experiments the identified parameters are used as initial values to be improved with numerical modelling. The simulation results make evident that this easy-to-use program can be a fundamental tool not only for modellers but for experimental working groups also.

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Jan Studzinski, Olgierd Hryniewicz (Editors)

**MODELLING CONCEPTS AND DECISION
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This book presents the papers that describe the most interesting results of the research that have been obtained during the last few years in the area of environmental engineering and environment protection at the Systems Research Institute of the Polish Academy of Sciences in Warsaw and the Leibniz-Institute of Freshwater Ecology and Inland Fisheries in Berlin (IGB). The papers were presented during the First Joint Workshop organized at the IGB in February 2006. They deal with mathematical modeling, development and application of computer aided decision making systems in the areas of the environmental engineering concerning groundwater and soil, rivers and lakes, water management and regional pollution.

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