

## Mapping regions of equifinality in the parameter space

*A method to evaluate inverse estimates and to plan experimental boundary conditions*

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### Abstract & Introduction

Breakthrough curves (BTCs) of column outflow experiments are frequently used to identify parameters of reactive transport in porous media. However, inverse techniques are often connected with uniqueness problems, i.e. more than a single parameter set can reproduce the breakthrough curve equally well – a problem, which is termed equifinality (Beven, 1993). In studies considering reactive transport, the two-site two-region model is applied frequently to explain the observed behavior of organic and inorganic substances (Streck *et al.*, 1995; Wehrer and Totsche, 2008). However, it appears that in particular the parameter set, which describes the nonequilibrium transport, is prone to equifinal solutions (Koch and Flühler, 1993; Wehrer and Totsche, 2008). Thus, the aim of this study was to investigate the regions in the parameter space where equifinal solutions of the parameter set non-equilibrium sorption coefficient  $K_{neq}$ , mass transfer rate  $r$  and initial concentration at nonequilibrium sites  $S_{ini}$  are likely. This should serve in the long run to be able to evaluate the reliability of inversely gained parameters and to optimize column experiments for inverse parameter estimation. Forward simulations with systematically varied parameters and boundary conditions were carried out and

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the numerically produced BTCs were compared with each other. This way a map of the parameter space could be delineated, which shows where parameters are reliable and which types of equifinality problems occur.

### Methods

#### *Theoretical background*

The extent of the non-equilibrium in column experiments is a function of the mass-transfer time-scale and the transport time-scale. The product mass transfer rate and retardation coefficient  $r^*R$  represents the reaction time scale of mass-transfer.  $R$  is related to the sorption coefficient  $K$  by  $R=1+K\rho/\theta$  with  $\rho$ : bulk density [ $M^*L^{-3}$ ] and  $\theta$ : water content. The ratio of the mean pore water velocity  $v$  [ $L^*T^{-1}$ ], and the column length  $L$  [ $L$ ], defines the transport time scale. The smaller the ratio of mass-transfer to transport time scale, the larger is the extent of non-equilibrium. Flow interruptions can be used to measure the extent of the non-equilibrium (Brusseau *et al.*, 1997; Wehrer and Totsche, 2003). The prolonged residence time during no-flow conditions allows the system to proceed towards equilibrium. When the substance is present in the solid phase initially and the column is eluted with a substance-free input solution, the concentration in the pore water will rise while the flow is interrupted. The observed concentration step at the column outlet after flow is resumed is increasing for increasing non-equilibrium.

#### *Model*

The BTCs were simulated with the numerical code RICHY (Prechtel *et al.*, 2002). This code is based on the advection-dispersion equation combined with kinetically controlled (non-)linear sorption implemented with a first-order mass-transfer.

$$\partial_t(\theta C) - \nabla(D\nabla C - qC) + \rho_b \partial_t(f_{eq} K_{eq} C^n + f_{neq} S(C)) = 0$$
$$\partial_t S = r(K_{neq} C^m - S)$$

with  $t$  [T] time,  $\theta$  [-] water content,  $C$  [ $M^*L^{-3}$ ] aqueous concentration,  $D$  [ $L^2*T^{-1}$ ] dispersion,  $q$  [ $L^*T^{-1}$ ] water flow,  $\rho_b$  [ $M^*L^{-3}$ ] bulk density,  $f_{eq}$  [-] mass fraction of equilibrium sorption sites,  $K_{eq}$  [ $L^3*M^{-1}$ ]

equilibrium sorption coefficient,  $n$  [-] and  $m$  [-] Freundlich-exponents,  $f_{\text{neq}}$  [-] mass fraction of non-equilibrium sorption sites,  $S$  [-] solid phase concentration,  $r$  [ $\text{T}^{-1}$ ] mass transfer rate,  $K_{\text{neq}}$  [ $\text{L}^3 \cdot \text{M}^{-1}$ ] non-equilibrium sorption coefficient.

### Scenarios

Boundary conditions and parameters were varied in a systematical way: four types of numerical experiments were tested with variations of flow velocity and duration of percolation intervals (Table 1). The standard scenario is based on the results of real world experiments (Wehrer and Totsche, 2008) and shall serve for evaluation of the parameters gained there. The scenario “fast flow” has a flow velocity 5 times that of the standard scenario. Such experiments were also conducted by Wehrer and Totsche (2008). The scenario “long PI” has percolation intervals with a duration of 5 times of those of the standard scenario and the scenario “CEN/TS” refers to the boundary conditions prescribed in the European norm for upflow percolation experiments CEN/TS 14404 (CEN, 2002). The parameters non-equilibrium sorption coefficient  $K_{\text{neq}}$  and rate parameter  $r$  were varied within intervals representing a wide range of properties of potential target compounds in different matrices (Table 2). The initial concentration at non-equilibrium sites  $S_{\text{ini}}$  was also considered as parameter which need to be fitted to reproduce experimental BTCs (Wehrer and Totsche, 2008).

Table 1: Scenarios of boundary conditions of the numerical experiments

boundary condition	stand ard	fast flow	long PI <sup>1)</sup>	CEN/ TS
flow velocity [ $\text{cm} \cdot \text{d}^{-1}$ ]	14	70	14	15
initial no flow [d]	0.3	0.3	0.3	3.3
1 <sup>st</sup> PI [d]	2	0.4	10	40
1 <sup>st</sup> FI <sup>2)</sup> [d]	3	3	3	-
2 <sup>nd</sup> PI [d]	16	0.2	5	-
2 <sup>nd</sup> FI [d]	1	1	1	-
3 <sup>rd</sup> PI [d]	1	0.2	5	-
total [d]	8.3	5.1	24.3	43.3

1) PI: percolation intervals

2) FI: flow interruptions

Table 2: Constant and varied parameters of the transport model

parameter	interval	step
$\rho$ [ $\text{g}/\text{cm}^3$ ]	2	
$n$ [-]	0.25	
$\lambda$ [cm]	1	
$D$ [ $\text{m}^2/\text{s}$ ]	$1 \cdot 10^{-9}$	
$C_{\text{ini}}$ [mg/l]	0	
$S_{\text{ini}}$ [mg/kg]	$8 \cdot 10^{-6}$ - $1 \cdot 10^{-3}$	5
$K_{\text{eq}}$ [l/kg]	0	
$K_{\text{neq}}$ [l/kg]	$5 \cdot 10^{-2}$ - $5 \cdot 10^{+2}$	$\sqrt{5}$
$r$ [1/d]	$1 \cdot 10^{-5}$ - $1 \cdot 10^{+2.5}$	$\sqrt{5}$

### Evaluation of breakthrough curves

Although two BTCs may be not equal in a mathematical sense, in the way that each concentration at each time step is equal within the numerical accuracy of the simulation, they may be so close to each other that they are indiscernable due the white noise of the experiment. Based on the results of Wehrer and Totsche (2008), two BTCs were classified as identical, when their root mean square deviation (RMSD) was lower than 4% of their mean concentration.

### Results and Discussion

In Figure 1, a map of equifinalities is drawn for the standard scenario in the parameter space of  $r$  and  $R$  with  $S_{\text{ini}} = 2 \cdot 10^{-4}$  mg/kg. The regions of equifinality are divided into 5 classes. In each class certain parameters or ratios of parameters have to remain equal that equal BTCs can be produced while other parameters may be different. Of course, the parameters, which may be different cannot be identified uniquely within that region – the model is insensitive to this parameter. In contrast, the model is sensitive to parameters or parameter ratios, which have to remain equal. The classes are described as follows:

1: no equifinality; each parameter set produces a unique solution.

2: Insensitivity to changes of  $K_{\text{neq}}$ ,  $r$  and  $S_{\text{ini}}$ , if the reaction time scale  $r \cdot R$ , the equilibrium concentration of nonequilibrium sites  $S_{\text{ini}}/K_{\text{neq}}$ , and the product  $S_{\text{ini}} \cdot r$  remain equal.

- 4: Insensitivity to  $K_{neq}$ ,  $r$  and  $S_{ini}$ , sensitivity to the product  $S_{ini} \cdot r$ .
- 5: Insensitivity to  $r$ , sensitivity to  $K_{neq}$  and  $S_{ini}$  (and their ratio).
- 6: Insensitivity to  $K_{neq}$ ,  $r$  and  $S_{ini}$ , sensitivity to  $S_{ini}/K_{neq}$ .

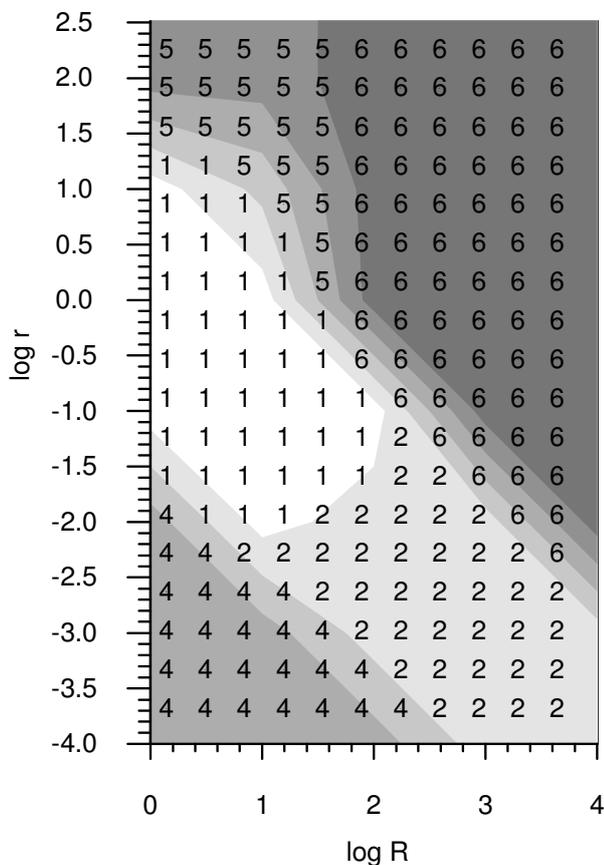


Figure 1: regions of equifinality of the standard scenario. Explanation: see text.

Each of the regions can be attributed to a different type of BTC (Figure 2). The transition from one type to another is gradually. Class-5-region BTCs show no reaction to flow interruptions – the system is at equilibrium and thus the mass transfer rate can't be identified. Region 6 has BTCs with a constant outflow concentration and no reactions to flow interruptions. Such a BTC can be attributed to different  $K_{neq}$ ,  $r$  and  $S_{ini}$ , as long as  $S_{ini}/K_{neq}$  is constant. The reason is that within the experimental duration not sufficient mass is leached from the column to result in a significant reduction of the outflow concentration due to low ratios of  $S_{ini}/K_{neq}$ . Class 2 and 4 BTCs also have constant outflow concentrations under steady state conditions (due to the named reason), but they show reactions on imposed flow

interruptions. Although the BTCs are insensitive to parameter changes some information can still be gained from class 2 BTCs, because equal BTCs are only produced for equal mass transfer time scales and equal ratios of  $S_{ini}/K_{neq}$ . Thus with little more information – for example the initial concentration – it is possible to identify the relevant parameters. Only class-1-BTCs can be attributed uniquely to one set of parameters. They show a decrease of concentration over time and reactions to flow interruptions.

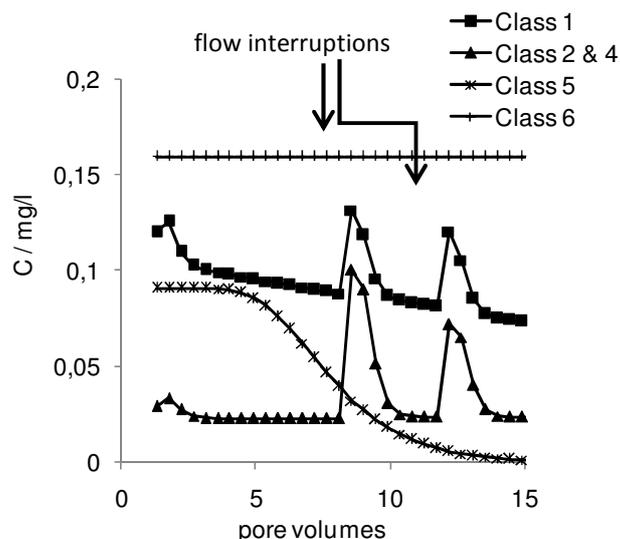


Figure 2: types of breakthrough curves for the standard scenario

The regions of equifinality also depend on the boundary conditions of the experiment. Figure 3 shows how the region of unique parameter estimation varies, depending on the scenario. Fast flow results in a shift of this region towards faster mass transfer rates (Figure 3a) because the system is forced into stronger nonequilibrium. Thus, faster rates can be identified but this goes on the expense of very slow rates, where the model becomes insensitive. On the contrary, longer percolation intervals (Figure 3b, scenario "long PI") allow the identification of larger retardation coefficients at slower rates, because more of the initial mass is leached from the column, resulting in a significant decrease of the outflow concentration at steady state. A column experiment with boundary conditions of the CEN/TS 14404 performs little worse than the scenario "long PI", due

to the lack of a second flow interruption. Also, such an experiment requires double the time than the scenario "long PI" (Table 1) and 5 times longer than the standard scenario. Moreover, the CEN/TS 14404 places the flow interruption at the beginning of the experiment.

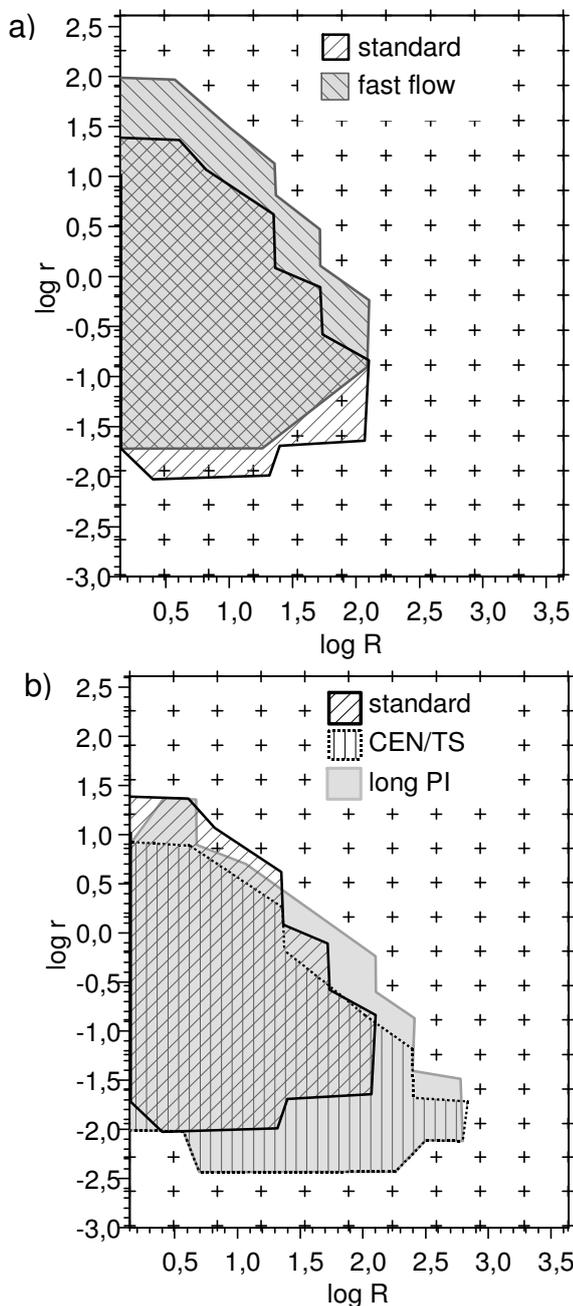


Figure 3: regions of unique parameter estimation of a) the fast flow- and the standard scenario and b) the CEN/TS-, the long percolation interval- and the standard scenario.

As already denoted in Wehrer and Totsche (2008), during that period outflow concentrations of alkaline mineral wastes are dominated by easily soluble salts,

which may not be representative of the long term leaching behavior.

## Conclusions

It was found that on the one hand, regions of uniqueness depend on the boundary conditions of the experiment. Consequently, if the correct experimental boundary conditions – such as flow velocity, number and duration of percolation intervals and flow interruptions – are chosen, uniqueness problems can be avoided *a priori*. All what is required are some a priori information on the target compounds and materials and maps of regions of uniqueness for different experimental designs. On the other hand parameter estimates can be plotted into such maps *a posteriori*, to be able to evaluate whether equifinal solutions exist.

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