Preselection of a sorption model based on a column test: the algorithm and an example of its application

Marek Marciniak¹ · Monika Okońska¹ · Mariusz Kaczmarek²

Received: 2 March 2020 / Accepted: 19 March 2021 / Published online: 28 April 2021
© The Author(s) 2021

Abstract

In order to describe the contamination of saturated porous media, it is necessary to find an appropriate mathematical model that includes processes occurring in aquifers, such as advection, dispersion, diffusion, and various kinds of sorption. The identification of parameters of those processes is possible through laboratory column experiments, which result in records of breakthrough curves for a conservative tracer and a reactive tracer. An algorithm leading to the preliminary selection of the mathematical model that best describes transport processes of the reactive tracer in the experimental column is proposed in this article. A study published previously presented a sensitivity analysis for an arbitrarily adopted variability of the transport parameters. The analysis involved examining changes in the shape of breakthrough curves caused by the alteration of each parameter value. Specially defined indicators called descriptors were proposed to quantitatively describe the breakthrough curves. Then, formulas were proposed to determine the percentage deviations of descriptors of the breakthrough curve obtained for the reactive tracer in relation to the descriptors of the breakthrough curve of the conservative tracer. In the work described in this article, the deviations are analyzed and an algorithm is proposed that allows the preselection of the most suitable sorption model out of the five discussed simple (one-site) and six hybrid (two-site) models. The algorithm can facilitate and accelerate the interpretation of column experiments of contaminant transport in a porous medium. An example is provided to illustrate the usability of the proposed algorithm.

Keywords Laboratory experiments · Contamination · Sorption models · Model selection

Introduction

Due to increasing human impact on the environment, more contaminants are reaching aquifers and causing deterioration of groundwater quality (Kleczkowski 1984; Appelo and Postma 1999; Dragon 2006; Bear and Cheng 2010; Witczak et al. 2013). It is necessary not only to investigate the processes of contaminant transport, but also forecast the fate of contaminants in the subsurface (Johnson et al. 2003). Forecasting contaminant transport in aquifers requires the formulation of an adequate mathematical model and identification of the model parameters. The mathematical description of such

transport has been evolving, starting from the 1970s. Initially, sorption isotherm models were analyzed, which lead to the development of experimental methods focusing on these isotherms (Limousin et al. 2007). Nowadays, reactive transport models are essential to investigate related physical, chemical and biological processes (Lichtner et al. 1996). These models are associated with constitutive laws and assume conservation of energy, momentum and solute mass (Steefel et al. 2005). Lichtner et al. (1996) highlights that the continuum hypothesis underlies theoretical considerations concerning transport in aquifers. It is assumed that a physical system can be approximated by a mathematical model of continuous media and the properties of the system change smoothly enough to use calculus and related numerical tools to describe transport processes. Such an assumption makes it possible to analyze the dynamics and kinetics of the system using partial differential equations.

Transport processes can be analyzed on various time and spatial scales. The mathematical models of dynamically occurring processes can be verified during column experiments,

✉ Marek Marciniak
mmarc@amu.edu.pl

¹ Institute of Physical Geography and Environmental Planning, Adam Mickiewicz University in Poznań, Poznań, Poland

² Department of Mechatronics, Kazimierz Wielki University in Bydgoszcz, Bydgoszcz, Poland

using columns of various sizes (Liu et al. 2008). On the other hand, processes occurring on the geological time-scale, especially diffusion processes, are more difficult to verify (Steefel and Lichtner 1994). The upscaling of results from the column scale to the local or regional scale in the field is a separate problem. Bear and Cheng (2010) presented a synthetic overview of water balance modelling, groundwater flow and contaminant transport.

In order to describe the transport of pollutants in a sand deposit, it is necessary to recognize the hydrogeochemical conditions. The hydraulic conductivity and the hydraulic gradient are of most importance for the transport of pollutants in the sand deposit (Zhu 2019). The geological properties are determined by the lithology of the deposit and the content of clay fraction and organic materials. The chemical composition of the water as well as the type and concentration of the pollutant are also important factors (Appelo and Postma 1999; Fetter 2001).

The analysis of the hydrogeochemical conditions alone may not provide unambiguous information about the processes occurring in the case of transporting a specific pollutant in the investigated sand deposit (Dai et al. 2012). For the recognition of processes occurring during a column experiment, it may be helpful to analyze the recorded breakthrough curve of the reactive tracer and compare it with the recorded breakthrough curve of the conservative tracer.

Transport analyses are most often conducted in laboratory conditions, less often in the field. Laboratory column experiments are performed using conservative and reactive tracers (Fetter 1999; Małeckı et al. 2006; Liu et al. 2008; Lin et al. 2019). As a result, breakthrough curves for both types of tracers are obtained. The selection of the transport model requires choosing an appropriate mathematical description of the processes taking place, particularly an adequate sorption model for the deposit, which will generate breakthrough curves for conservative and reactive tracers with a high goodness of fit. The current practice in the selection of the mathematical model of sorption relies on choosing a certain group of models—hereinafter this procedure will be called qualitative preselection. Next, the effectiveness of these models is compared in terms of accordance between the model predictions and the observation results, which is the basis for the proper selection. Methods of model preselection used so far are based on qualitative criteria such as the identification of physical and chemical mechanisms of sorption for the investigated deposit and the migrating substances (an adequacy criterion) and on the basis of the simplicity criterion (Limousin et al. 2007).

The proper selection involves assessing the goodness of fit between calculated and experimental breakthrough curves through measures or statistical tests (Saiers and Hornberger 1996). Koeppenkaströpt and De Carlo (1993) mention several adequate statistical indicators such as the standard deviation, coefficient of determination, correlation coefficient, and an

index called the model selection criterion (MSC). The last one, besides characterizing the goodness of fit, also represents the information contained in a set of parameters of each model, and takes into account the ratio of the number of model parameters to the number of experimental data.

When selecting the best model, the parameters of all preselected models should be identified; furthermore, for each preselected model the goodness of fit should be determined. With this approach, selecting the appropriate model is laborious and time consuming, especially when dealing with poorly examined aquifers where the transport of unknown contaminants takes place and the existing physical, chemical and biological parameters are not recognized. Despite an extensive study, no other methods of selecting the adequate transport model have been found in the literature available to the authors. The complexity of transport processes and the variety of the proposed models make the selection of the transport model difficult, thus justifying the search for tools supporting the selection process.

The aim of the presented research was to develop an algorithm which, on the basis of quantitative measures (descriptors) of breakthrough curves, enables a significant narrowing down of the number of model groups that should undergo proper selection. The authors focused on analyzing impulse breakthrough curves for a reactive tracer in relation to the curves for a conservative tracer.

This new approach to the issue of preselection relies on the use of descriptors for both breakthrough curves, therefore it was called ‘quantitative preselection’. The development of the algorithm was based on a parametric analysis of breakthrough curves. The variability range of transport parameters adopted in the analysis corresponded to the variability of these parameters in natural hydrogeological conditions. In the initial stage of research, six descriptors which quantify changes in the shape of breakthrough curves were analyzed. The quantitative preselection algorithm of the transport model based on breakthrough curve descriptors was initially limited to a set of five simple sorption models (Okońska et al. 2019b) or six hybrid models (Okońska et al. 2019a). Ultimately, it turned out that for an effective quantitative preselection of a model from a set of five simple models and six hybrid models, it is sufficient to analyze three descriptors.

The algorithm proposed in this article facilitates and accelerates the selection of the best mathematical model of transport processes taking place during the column experiment. The algorithm also objectifies the model selection thanks to the use of breakthrough curve descriptors without the need to analyze the molecular mechanisms of sorption. It should be noted that the proper selection of a transport model, apart from statistical tests which determine theoretical and experimental curve fitting, must also include the expertise of a hydrogeologist, who always makes the final decision related to the model selection. The usefulness of the quantitative preselection

algorithm of the transport model is illustrated on the example of a water intake located in the Prosna River valley, Poland.

Methods

Column experiment

The column experiment involves the flow of water and solutes through a column filled with sand (Domenico and Schwartz 1998; Liu et al. 2017). First, water flows in the experimental column until there is hydrochemical stabilization of the sand deposit, which can be manifested by the stabilization of electrical conductivity at the outflow; after that, water with tracers is injected. Usually, the simultaneous injection of a conservative tracer (only transported by means of advection, diffusion and dispersion) and a reactive tracer (additionally subject to sorption processes) is executed as an impulse with the duration of t_{in} (Fig. 1; see Appendix for a summary of the nomenclature).

The injection of tracers is described by the injection curve $C_{in}(t)$, which shows the changes in tracer concentration over time at the input of the column (Fig. 1). Curves depicting the change of conservative and reactive tracer concentrations over time $C_{out}(t)$, referred to as breakthrough curves, are recorded at the column output.

The dimensions of columns are significant in column experiments. It is important that the relation of the diameter D to the length L of the column provides a representative sample and minimal wall effects. Liu et al. (2008) conducted experiments using columns with the following dimensions: $D = 3.4$ cm, $L = 10$ cm to $D = 15$ cm, $L = 80$ cm. Analyzing the experiences of other authors and taking into account previous research conducted by the authors, columns with intermediate dimensions were used. In the presented example, a $D = 9$ cm, $L = 50$ cm column was used, which can be considered sufficiently

representative for the investigation of transport processes. Moreover, the structure of the sand deposit is also important. It should be noted that analyzing undisturbed sand samples may seem unrealistic. On the other hand, a uniformly grained deposit prepared by selecting appropriate grains hardly reflects natural conditions; therefore, in the presented research, deposits containing grains of a natural range of sizes were tested.

Mathematical models

The transport of the conservative tracer in a porous medium involves processes such as advection, diffusion and dispersion. In addition, the reactive tracer is also subject to equilibrium or nonequilibrium sorption processes. Generally, one-dimensional (1D) transport of the tracer subject to transport processes is represented by the following equation (Luckner and Schestakow 1991; Weber Jr et al. 1991; Lichtner 1996):

$$\frac{\partial C}{\partial t} = -\frac{k \cdot i}{n_e} \frac{\partial C}{\partial x} + \left(D_M + \alpha \frac{k \cdot i}{n_e} \right) \frac{\partial^2 C}{\partial x^2} - (1-n) \frac{\rho_s}{n_e} \frac{\partial s}{\partial t} \quad (1)$$

where the following terms are as defined:

C	Tracer concentration in the liquid phase [$M L^{-3}$]
D_M	Coefficient of diffusion molecular [$L^2 T^{-1}$]
i	Hydraulic gradient [$L L^{-1}$]
k	Hydraulic conductivity [$L T^{-1}$]
n	Total porosity [–]
n_e	Effective porosity [–]
s	Tracer concentration in the solid phase (total sorbed-phase concentration) [$M M^{-1}$]
t	Time [T]
x	Distance [L]
α	Longitudinal dispersivity [L]
ρ_s	Density of the porous medium [$M L^{-3}$]

Fig. 1 Schematic diagram of a column experiment

This equation does not involve complex chemical reactions with the soil, biodegradation, chemi- and electro-osmotic processes or capillary effects.

In the case of the conservative tracer, the last component of Eq. (1) is left out, as sorption does not occur (model A-D). In the case of the reactive tracer, the last component of Eq. (1) refers to sorption processes, whose mathematical descriptions may display various levels of complexity (Kaczmarek and Kazimierska-Drobny 2007). Simple transport models with equilibrium sorption include so-called sorption isotherms:

- Linear Henry model (H model)

$$s = K_H C \quad (2)$$

where K_H is the Henry distribution coefficient [$L^3 M^{-1}$]

- Nonlinear Freundlich model (F model)

$$s = K_F C^{n_F} \quad (3)$$

where K_F is the Freundlich sorption coefficient [$L^3 M^{-1}$] and n_F is the Freundlich sorption exponent [-].

- Nonlinear Langmuir model (L model)

$$s = \frac{\alpha_L \beta_L C}{1 + \alpha_L C} \quad (4)$$

where α_L is the Langmuir constant [$L^3 M^{-1}$] and β_L is the total sorption capacity of the solid phase [$M M^{-1}$].

The simple kinetic transport models with non-equilibrium sorption are:

- Linear irreversible sorption model (I model)

$$\frac{\partial s}{\partial t} = k_1 C \quad (5)$$

where k_1 is the irreversible sorption rate coefficient [$L^3 M^{-1} T^{-1}$]

- Linear reversible sorption model (R model)

$$\frac{\partial s}{\partial t} = k_2 C - k_3 s \quad (6)$$

where k_2 is the first reversible sorption rate coefficient [$L^3 M^{-1} T^{-1}$] and k_3 is the second reversible sorption rate coefficient [T^{-1}].

The mathematical model describing 1D advection-dispersion transport with sorption is a system of two equations, i.e., the transport Eq. (1) and the sorption Eqs. (2)–(6) (Marciniak et al. 2009). In the case of equilibrium sorption, these would be Eq. (1) and one of the following: Eq. (2), Eq. (3) or Eq. (4). For nonequilibrium sorption, these would be Eqs. (1) and (5) or Eq. (6).

Sorption processes occurring during the transport of the reactive tracer through porous media in natural geological settings are often more complex than it appears from the simple mathematical description of equilibrium or nonequilibrium sorption (Liu et al. 1991; Johnson et al. 2003; Maraqa 2007; Yu et al. 2019). In the macroscopic sense, equilibrium sorption may occur on some parts of the surface of soil grains while nonequilibrium sorption may occur on the other part of the soil grain surface (Van Genuchten and Wierenga 1976). Tracer concentration in the solid phase throughout equilibrium sorption was denoted as s_e , and tracer concentration in the solid phase throughout nonequilibrium sorption as s_n . In that case, instead of Eq. (1) combined with one of the simple sorption models, i.e. Eqs (2)–(6), a system of Eqs. (7), called the hybrid model, should be considered:

$$\begin{cases} \frac{\partial C}{\partial t} = -\frac{k \cdot i}{n_e} \frac{\partial C}{\partial x} + \left(D_M + \alpha \frac{k \cdot i}{n_e} \right) \frac{\partial^2 C}{\partial x^2} - (1-n) \frac{\rho_s}{n_e} \frac{\partial s}{\partial t} \\ s = s_e + s_n \end{cases} \quad (7)$$

where the equilibrium component s_e and nonequilibrium component s_n are described by one of the six hybrid models:

- Henry and linear irreversible sorption model (H-I model)

$$\begin{cases} s_e = K_H C \\ \frac{\partial s_n}{\partial t} = k_1 C \end{cases} \quad (8)$$

- Freundlich and linear irreversible sorption model (F-I model)

$$\begin{cases} s_e = K_F C^{n_F} \\ \frac{\partial s_n}{\partial t} = k_1 C \end{cases} \quad (9)$$

- Langmuir and linear irreversible sorption model (L-I model)

$$\begin{cases} s_e = \frac{\alpha_L \beta_L C}{1 + \alpha_L C} \\ \frac{\partial s_n}{\partial t} = k_1 C \end{cases} \quad (10)$$

- Henry and linear reversible sorption model (H-R model)

$$\begin{cases} s_e = K_H C \\ \frac{\partial s_n}{\partial t} = k_2 C - k_3 s_n \end{cases} \quad (11)$$

- Freundlich and linear reversible sorption model (F-R model)

$$\begin{cases} s_e = K_F C^{n_F} \\ \frac{\partial s_n}{\partial t} = k_2 C - k_3 s_n \end{cases} \quad (12)$$

- Langmuir and linear reversible sorption model (L-R model)

$$\begin{cases} s_e = \frac{\alpha_L \beta_L C}{1 + \alpha_L C} \\ \frac{\partial s_n}{\partial t} = k_2 C - k_3 s_n \end{cases} \quad (13)$$

To solve the transport equations, the authors adopted the impulse injection, for which appropriate boundary conditions were defined. The initial condition referred to the zero concentration of the substance in the whole analyzed volume at the initial time $t = 0$:

$$C(x, t = 0) = 0 \text{ for } x \geq 0 \quad (14)$$

At the column input, Dirichlet's boundary condition was imposed in the form of an impulse injection with amplitude C_0 and duration t_{in} :

$$\begin{cases} C(x = 0, t) = C_0 & \text{for } 0 < t \leq t_{in} \\ C(x = 0, t) = 0 & \text{for } t > t_{in} \end{cases} \quad (15)$$

At the column output, Neumann's boundary condition was imposed in the following form:

$$\left. \frac{\partial C(x, t)}{\partial x} \right|_{x=L} = 0 \text{ for } t \geq 0 \quad (16)$$

Descriptors

In order to investigate the impact of the changes in model parameter values on the shape of the breakthrough curves, the authors conducted a sensitivity analysis for all eleven models of pollutant transport in a saturated porous medium (Okońska et al. 2019a, b). The analysis was conducted for 12 parameters of water flow and tracer transport in the filtration column. The basic values of each parameter, as well as the range of their variability from the lower to the higher values were determined on the basis of a literature review (Table 1). The lower and higher values were chosen to correspond to the actual variability of these parameters occurring during the transport of both conservative and reactive tracers in natural hydrogeological settings.

Six descriptors were used in the sensitivity analysis stage to quantify the breakthrough curves. When looking for a solution to the problem of transport model preselection, it was found that the number of descriptors can be limited to three. For the quantitative characterization of the shape changes of the breakthrough curves, the authors used the following three descriptors:

- Relative tracer recovery ε [%]:

$$\varepsilon = \frac{100}{C_0 t_{in}} \int_{t_1}^{t_2} C(t) dt \quad (17)$$

where time t_1 was determined from the breakthrough curve $C(t)$ as the last moment at which $C(t_1) < 0.01 \cdot C_0$, whereas time t_2 was determined from the breakthrough curve $C(t)$ as the first moment at which $C(t_2) < 0.01 \cdot C_0$

- Time of maximum tracer concentration at the output t_{max} [min]:

$$t_{max} = t|_{C=C_{max}} \quad (18)$$

where C_{max} is the maximum tracer concentration at the output

- Spread of breakthrough curve σ [min]:

$$\sigma = \sqrt{\frac{\int (t - t_{max})^2 C(t) dt}{\int C(t) dt}} \quad (19)$$

The meaning of all symbols present in definitions of descriptors for the conservative and reactive tracers are illustrated in Fig. 2. Detailed results showing the influence of model parameters on breakthrough curves, as well as descriptor values for the conservative and reactive tracers, were presented in Okońska et al. 2019a, b.

Relative changes in the values of the three descriptors defined previously, determined for breakthrough curves of the reactive tracer and the conservative tracer, were calculated as percentage deviations δD :

$$\delta D = \frac{D_r - D_c}{D_c} 100\% \quad (20)$$

where D is one of the descriptors ε , t_{max} and σ are defined by Eqs. (17)–(19), D_r is the descriptor value for the breakthrough curve of the reactive tracer, D_c is the descriptor value for the breakthrough curve of the conservative tracer.

Results

Algorithm of sorption model preselection

The results of the parametric analysis in the form of calculated percentage deviations δD are presented in tables as bar graphs for simple models (Fig. 3) and for hybrid models (Figs. 4 and 5). The third columns of the tables contain the lower, basic and higher parameter values. The percentage deviations of the descriptors in the range from -100 to 300% are depicted in columns 4, 5 and 6. Table rows include parameter values that correspond with particular models in the range provided in Table 1.

For each model the descriptors whose percentage deviations in the conducted sensitivity analysis for all the considered parameters or combinations of sorption parameters exceed 5% highlighted. The assumed value of deviation results

Table 1 Variability range of hydrogeological parameters assumed for the transport processes, based on Okońska et al. (2019b)

Transport parameters	Symbol	Unit	Parameter's value			References
			Lower	Basic	Higher	
Filtration parameters						
Hydraulic conductivity	k	m s^{-1}	5.0×10^{-5}	1.0×10^{-4}	5.0×10^{-4}	Appelo and Postma 1999
Effective porosity	n_e	—	0.27	0.30	0.33	Domenico and Schwartz 1998
Diffusion and dispersion parameters						
Diffusion coefficient	D_M	$\text{m}^2 \text{s}^{-1}$	1.0×10^{-9}	5.0×10^{-9}	1.0×10^{-8}	Maraqa 2007
Longitudinal dispersivity	α	m	0.008	0.010	0.020	Dubus et al. 2003 Maraqa 2007
Sorption parameters						
Henry distribution coefficient	K_H	$\text{dm}^3 \text{kg}^{-1}$	0.005	0.010	0.020	Fohrmann et al. 2001 Maraqa and Khashan 2014
Freundlich sorption coefficient	K_F	$\text{dm}^3 \text{kg}^{-1}$	0.005	0.010	0.020	Khan et al. 2010
Freundlich sorption exponent	n_F	—	0.6	0.8	1.0	Dubus et al. 2003 Maraqa 2007
Langmuir constant	α_L	$\text{dm}^3 \text{mg}^{-1}$	0.04	0.07	0.10	Barrow 1978
Total sorption capacity of the solid phase	β_L	mg kg^{-1}	1.0	1.2	1.4	Ahmed et al. 2011
Irreversible sorption rate coefficient	k_1	$\text{dm}^3 \text{kg}^{-1} \text{s}^{-1}$	1.0×10^{-6}	5.0×10^{-6}	1.0×10^{-5}	Wehehan et al. 2007
First reversible sorption rate coefficient	k_2	$\text{dm}^3 \text{kg}^{-1} \text{s}^{-1}$	1.0×10^{-6}	5.0×10^{-6}	1.0×10^{-5}	Liu et al. 1991
Second reversible sorption rate coefficient	k_3	s^{-1}	1.0×10^{-4}	2.0×10^{-4}	4.0×10^{-4}	Wehrhan et al. 2007 Liu et al. 1991

from the estimation of measurement uncertainties related with the execution of column experiments. Then, the baseline (minimum) δD_b values were determined for percentage deviations of descriptors: $\delta \varepsilon_b = 5\%$, $\delta t_{\max b} = 15\%$ and $\delta \sigma_b = 15\%$. The percentage deviation thresholds of the individual descriptors must be greater than the uncertainties associated with the measurement of the breakthrough curves. The proposed algorithm verifies if critical descriptor values were exceeded (in the following order: $\delta \varepsilon_b$, $\delta t_{\max b}$ and $\delta \sigma_b$). Since the values of descriptors and their deviations may be determined from the experimental breakthrough curves, it was assumed that the

algorithm of model classification obtained as part of the sensitivity analysis can be applied to preselect the models of sorption for deposits and tracers occurring in natural settings. The resulting flowchart of the model preselection algorithm is presented in Fig. 6.

Example of column experiment and algorithm application

The municipal water intake is located in the Holocene river terrace of the Prosna River (Poland) in the town of Tursko and supplies water to the city of Pleszew (Fig. 7). The aquifer has a limited spatial extent. The lithology is dominated by river and glacial sediments of varying thickness ranging from a few to even 60 m. The near-surface zone, 5–10 m thick, is dominated by Holocene peat, silt and river sands of various grain size, dispersed with organic matter. In the deeper part of the aquifer, Pleistocene sands and gravels are present. The aquifer is unconfined and highly susceptible to pollution from the surface.

The water intake consists of three pumping wells and six observation wells. Under natural conditions, groundwater flows from the south and west towards the Prosna River. Pumping intensified the seepage from local streams and drainage ditches. One of the drainage ditches is used to transport water from the nearby sewage treatment plant in the town of Gołuchów. The seepage of partially treated sewage from the

Fig. 2 Symbols used in the description of descriptors: **a** the conservative tracer breakthrough curve; **b** the reactive tracer breakthrough curve

Fig. 3 The variability range of descriptor deviations for simple models

Fig. 4 The variability range of descriptors deviations for hybrid models with irreversible sorption

Fig. 5 The variability range of descriptor deviations for hybrid models with reversible sorption

Fig. 6 The algorithm of transport model selection based on the experimentally recorded breakthrough curve of the tracer. See text for symbol explanations

drainage ditch into the aquifer deteriorates the quality of groundwater (Dragon et al. 2016).

While drilling the P3 observation well (Fig. 7), a sample of medium-grained sand was taken from a depth of 7–8 m, from the zone where contaminants seeping from the drainage ditch are transported. This sample was used to perform a column experiment in order to determine the parameters of water flow and transport of selected ions. The column experiment involved recording the breakthrough curve for chloride ions (Cl), treated as a conservative tracer, and breakthrough curves for selected reactive tracers, i.e., lithium ions (Li), zinc ions (Zn), and copper ions (Cu) migrating through a sample of medium-grained sand (Fig. 8). The concentration of chloride ions in the water sample was determined using the ion chromatography (IC) method. The detection limit for those ions was 0.011 mg dm⁻³. The concentration of lithium ions, zinc and copper was determined by means of flame atomic absorption spectrometry (FAAS). The FAAS method is widely used

in research on the transport of pollutants in surface waters (Walna and Siepak 2012) and in groundwater (Ciążela et al. 2018). The detection limit for ions concentration was, respectively, 0.001 (Li), 0.002 (Zn) and 0.001 (Cu) mg dm⁻³.

The uniformity coefficient of the sand collected from the aquifer at the Tursko water intake was $U = 2.12$ ($d_{60} = 0.55$ mm; $d_{10} = 0.26$ mm). The coefficient U is defined as: $U = d_{60}/d_{10}$, where d_{10} is the grain diameter [mm] corresponding to 10% of the sample passing by weight (which means that 10% of the particles are smaller than the diameter d_{10}) and d_{60} is the grain diameter [mm] at 60% passing (Holtz and Kovacs 1981). Total organic carbon (TOC) content was 0.021%. Trace amounts (<0.01%) of the clay fraction were detected. Clay minerals identified in the sand sample were smectite, kaolinite and illite. The experimental column was filled with sand, taking care of saturation and the even distribution of the grains. For 2 days, filtration in column with water taken from the P3 observation well was carried out in order to obtain

Fig. 7 Groundwater intake in the Prosna River valey

hydrochemical stabilization of the sand deposit. The hydraulic conductivity of the examined deposit was determined using the Darcy formula, by measuring the water flow rates several times. The total porosity was determined using the volumetric method. At the input of the column, the solution was injected as an impulse for 115 min. At the output of the column, samples of water were collected in chemically neutral vessels for 24 h. In this way, the breakthrough curves for each analyzed ion were obtained. These curves are shown in Fig. 8, as well as in Fig. 9a–d. More details about the methodology of implementing the column experiment can be found in the works of Marciniak et al. (2009) and Okońska et al. (2017).

To calculate the values of descriptors which characterize the shape of experimental breakthrough curves, the authors used the computation code *Descriptors2.m* written in the MATLAB environment (Okońska et al. 2019c). Then, percentage deviations of the descriptors were determined (Table 2). Next, in accordance with the proposed algorithm (Fig. 6, $\delta\varepsilon_b = 5\%$, $\delta t_{\max b} = 15\%$ and $\delta\sigma_b = 15\%$), mathematical models which best described tracer transport through the deposit were chosen for each analyzed ion. The previously analyzed baseline values of descriptor deviations δD_i were taken into consideration. An example of using the proposed

Fig. 8 Injection curve and experimental breakthrough curves for tracers: C/C_0 – tracer concentration in relation to its concentration in the injected solution

algorithm to select the model of copper ion transport is shown in Fig. 10.

The parameters of transport were identified using the *Id_Test_Kol4.m* code in the MATLAB environment. First, transport parameters were determined for the advection-dispersion model based on the breakthrough curve of chloride ions (Table 3). Then, the parameters that govern the transport of reactive ions were calculated for mathematical models chosen by the algorithm. These parameters are presented in Table 4. To identify the parameters, the authors used the numerical solutions of transport equations Eqs. (1)–(13) for the assumed boundary conditions (Eqs. 14–16) with the use of optimization methods implemented in the MATLAB environment (Okońska et al. 2017).

Matching of the numerically calculated breakthrough curves with the experimental curves for the models selected by the algorithm is presented in Fig. 9. The goodness-of-fit between numerical and experimental curves was established by calculating the root mean square error (RMSE) and the correlation coefficient r (Małeck et al. 2017).

Discussion

In order to check whether the proposed algorithm gives the best fitting transport model, the authors used the code *Id_Test_Kol4.m* to determine the parameter values of all sorption models considered in section ‘Mathematical models’ for the three reactive ions: lithium, zinc and copper. The five

Fig. 9 Fit of numerical breakthrough curves to experimental curves for the following ions: **a** chloride; **b** lithium; **c** copper; **d** zinc

Table 2 Values and percentage deviations of descriptors and selected transport models of specific ions

Tracer	ε [%]	$t_{\max}$ [min]	σ [min]	$\delta\varepsilon$ [%]	$\delta t_{\max}$ [%]	$\delta\sigma$ [%]	Model
Cl	99.7	346.0	45.7	0	0	0	A-D
Li	100.2	391.1	51.9	1	13	14	H or F
Cu	22.3	391.1	106.8	78	13	134	I or H-I or F-I
Zn	32.4	391.1	163.7	67	13	258	I or H-I or F-I

simple and the six hybrid mathematical models of sorption processes were tested. The results obtained for all the models are presented in Table 4. In the table, the models with the best fit, i.e., those with the lowest value of RMSE and the highest correlation coefficient r value, are highlighted with an asterisk. In addition, the model parameters indicated by the proposed algorithm are italic.

Fig. 10 An example of Cu ion transport model selection

The conducted research resulted in the following findings:

- For lithium (Li) ions the preselection algorithm proposed simple H and F models. The best fit between numerical and experimental breakthrough curves was obtained for the F, F-I and F-R models. The analysis of the identified parameter values shows that the differences between the breakthrough curves obtained from the F, F-I and F-R models are insignificant. In the hybrid models, the values of parameters k_1 , k_2 and k_3 are very low. This shows that equilibrium sorption is dominant in the process of lithium ion transport; therefore, the F model describes the process of lithium ions sorption with sufficient accuracy.
- For copper (Cu) ions and zinc (Zn) ions, the algorithm proposed a simple I model and hybrid H-I and F-I models. For these ions, both components of equilibrium and non-equilibrium sorption are significant. Goodness-of-fit indices, RMSE and r , prefer the F-I and F-R models.

Table 3 Identified parameters of the advection-dispersion model

Model	Parameter		Chloride ions		
	Symbol	Unit	Value	RMSE	<i>r</i>
A-D	<i>k</i>	m s ⁻¹	4.07×10^{-4}	0.241	1.00
	<i>n_e</i>	—	0.31		
	<i>D_M</i>	m ² s ⁻¹	0		
	<i>α</i>	m	0.0027		

However, the dominance of irreversible sorption is indicated by descriptor ε , which suggests that the recovery rate of copper and zinc ions is 22.3 and 32.4%, respectively.

Many authors have conducted research on the transport of Cu and Zn ions in groundwater. Krogulec and Zabłocki (2015) and Małeck et al. (2017) conducted research in the Kampinos National Park in Poland. They showed that the

mobility of copper and zinc in near-surface groundwater is a function of the lithology of the hypergenic zone. Both ions sorbed irreversibly, the process being more intense in the case of copper ions. Karathanasis (1999) conducted column experiments with soil colloids and showed that the presence of colloids typically enhanced metal transport by 5- to 50-fold over that of the control treatments, with Zn being consistently more mobile than Cu. Arias et al. (2005) studied the adsorption and desorption of Cu and Zn in the surface layers of acidic soils. Both for copper and zinc ions, better fit was obtained in the case of the Freundlich equation than the Langmuir equation. Arias et al. (2005) only focused on simple sorption models; however, they found higher adsorption than desorption both in arable soils and forest soils, which would suggest the conditions of irreversible sorption and confirm that the selection of F-I model was right.

Studies by various authors confirm the occurrence of irreversible sorption of Cu and Zn ions, which was also noticed in

Table 4 Values of parameters determined for the analyzed transport. The models with the best fit are highlighted with an asterisk (*); the model parameters indicated by the proposed algorithm (based on MATLAB) are *italic*

Model	Symbol	Unit	Li			Cu			Zn		
			Value	RMSE [mg dm ⁻³]	<i>r</i> [—]	Value	RMSE [mg dm ⁻³]	<i>r</i> [—]	Value	RMSE [mg dm ⁻³]	<i>r</i> [—]
H	<i>K_H</i>	dm ³ kg ⁻¹	2.16×10^{-2}	0.0668	0.990	3.40×10^{-2}	0.1729	0.926	3.58×10^{-2}	0.1467	0.927
F	<i>K_F</i>	dm ³ kg ⁻¹	$4.23 \times 10^{-3*}$	0.0347*	0.998*	2.52×10^{-2}	0.1730	0.937	2.85×10^{-2}	0.1470	0.927
	<i>n_F</i>	—	1.80*			1.20			1.18		
L	<i>α_L</i>	dm ³ mg ⁻¹	2.16×10^{-4}	0.0669	0.990	4.63×10^{-1}	0.1627	0.863	1.00×10^0	0.1173	0.831
	<i>β_L</i>	mg kg ⁻¹	99.90			2.28×10^{-1}			2.06×10^{-1}		
I	<i>k₁</i>	dm ³ kg ⁻¹ s ⁻¹	1.35×10^{-6}	0.2733	0.830	1.85×10^{-5}	0.0318	0.663	1.67×10^{-5}	0.0434	0.567
R	<i>k₂</i>	dm ³ kg ⁻¹ s ⁻¹	1.56×10^{-4}	0.0647	0.991	2.08×10^{-5}	0.0286	0.754	2.15×10^{-5}	0.0350	0.753
	<i>k₃</i>	s ⁻¹	7.25×10^{-3}			3.10×10^{-5}			7.00×10^{-5}		
H-I	<i>K_H</i>	dm ³ kg ⁻¹	2.16×10^{-2}	0.0668	0.990	2.82×10^{-2}	0.0119	0.958	3.22×10^{-2}	0.0171	0.943
	<i>k₁</i>	dm ³ kg ⁻¹ s ⁻¹	2.33×10^{-14}			1.58×10^{-5}			1.30×10^{-5}		
F-I	<i>K_F</i>	dm ³ kg ⁻¹	$4.23 \times 10^{-3*}$	0.0347*	0.998*	$2.16 \times 10^{-2*}$	0.0111*	0.964*	$2.85 \times 10^{-2*}$	0.0169*	0.944*
	<i>n_F</i>	—	1.80*			1.47*			1.18*		
	<i>k₁</i>	dm ³ kg ⁻¹ s ⁻¹	$2.22 \times 10^{-14*}$			$1.57 \times 10^{-5*}$			$1.30 \times 10^{-5*}$		
L-I	<i>α_L</i>	dm ³ mg ⁻¹	2.22×10^{-4}	0.0669	0.990	3.17×10^{-4}	0.0119	0.958	3.44×10^{-4}	0.0171	0.943
	<i>β_L</i>	mg kg ⁻¹	97.29			89.09			93.67		
	<i>k₁</i>	dm ³ kg ⁻¹ s ⁻¹	7.38×10^{-13}			1.58×10^{-5}			1.30×10^{-5}		
H-R	<i>K_H</i>	dm ³ kg ⁻¹	1.81×10^{-2}	0.0649	0.991	2.82×10^{-2}	0.0119	0.958	3.22×10^{-2}	0.0171	0.943
	<i>k₂</i>	dm ³ kg ⁻¹ s ⁻¹	1.47×10^{-4}			1.58×10^{-5}			1.30×10^{-5}		
	<i>k₃</i>	s ⁻¹	4.22×10^{-2}			2.22×10^{-14}			4.10×10^{-8}		
F-R	<i>K_F</i>	dm ³ kg ⁻¹	$4.23 \times 10^{-3*}$	0.0347*	0.998*	$2.16 \times 10^{-2*}$	0.0111*	0.964*	$2.86 \times 10^{-2*}$	0.0169*	0.944*
	<i>n_F</i>	—	1.80*			1.47*			1.17*		
	<i>k₂</i>	dm ³ kg ⁻¹ s ⁻¹	$2.22 \times 10^{-14*}$			$1.57 \times 10^{-5*}$			$1.30 \times 10^{-5*}$		
	<i>k₃</i>	s ⁻¹	$1.00 \times 10^{-4*}$			$2.10 \times 10^{-7*}$			$2.39 \times 10^{-7*}$		
L-R	<i>α_L</i>	dm ³ mg ⁻¹	1.04×10^{-4}	0.0650	0.991	2.94×10^{-4}	0.0119	0.958	3.44×10^{-4}	0.0171	0.943
	<i>β_L</i>	mg kg ⁻¹	83.76			96.24			93.57		
	<i>k₂</i>	dm ³ kg ⁻¹ s ⁻¹	6.28×10^{-5}			1.58×10^{-5}			1.30×10^{-5}		
	<i>k₃</i>	s ⁻¹	4.88×10^{-3}			4.37×10^{-14}			3.40×10^{-8}		

the area of the Tursko water intake. Therefore, the F-I model can be considered as aptly indicated by the proposed preselection algorithm.

Summary and conclusions

In order to investigate transport in a sand deposit during a column experiment, a qualitative preselection of sorption models was conducted, taking into consideration sorption mechanisms and model simplicity. As a result, a set of 11 models was obtained. For this set, a new algorithm that implements quantitative preselection has been proposed, which, in the authors' opinion, should precede and facilitate the proper selection of the best transport model.

A previously performed detailed parametric analysis and partial preselection algorithms that incorporate descriptors characterizing the geometry of breakthrough curves for conservative and reactive tracers served as the foundations of the proposed algorithm. Initially, a preselection algorithm was proposed for the five simple models (Okońska et al. 2019a), and then for the six hybrid models (Okońska et al. 2019b). In this study, the sorption model preselection algorithm was generalized with the joint consideration of simple and hybrid models using three breakthrough curve descriptors.

The starting points for the application of the algorithm are the experimentally recorded breakthrough curves of the conservative tracer and the reactive tracer. Next, the values of three descriptors D and percentage deviations of descriptors δD of the breakthrough curve of the reactive tracer in relation to the breakthrough curve of the conservative tracer should be calculated in accordance with the equations provided in this paper. Having the results of these calculations, the procedure is shown in Fig. 6. This algorithm will allow selection of the best fitting transport model. The usability of the proposed algorithm was confirmed by examples, one of which is presented in the article.

It must be stressed that the parametric analysis used as the basis for developing the proposed algorithm was conducted for a range of flow and transport parameters established by studying relevant existing literature. The issue that is worth exploring in further studies is the extension of the range of transport parameters adopted for the parametric analysis. This may result in the modification of the proposed baseline values of deviations of particular descriptors; furthermore, the conducted analysis refers to homogeneous media. A high diversification of the deposit grain sizes may be a factor disturbing the effectiveness of the algorithm. Broader application of the algorithm should show the influence of factors such as: the credibility of data derived from hydrogeological and hydrochemical exploration, the degree of hydrochemical complication of the transport process, soil gradation or the height of the deposit in the laboratory column.

It was demonstrated that the proposed algorithm can facilitate and accelerate the preselection of the best fitting transport model. The process of the proper model selection should be finalized by making the ultimate decision concerning the model choice. Such decision should always be made by the hydrogeologist interpreting the results of column experiments, who needs to take into consideration the hydrogeochemical determinants of contaminant transport in an investigated aquifer.

In the authors' opinion, the developed methodology of creating the quantitative preselection algorithm can be used for other sets of models (sorption models, but not only), other materials (with a different composition, soil structure or the type of liquid) and a different scale of transport processes. A broader implementation of the algorithm could improve the reliability of its predictions. Therefore, the authors provide the *Descriptors2.m* code in the electronic supplementary material (ESM), which enables the calculation of breakthrough curve descriptors.

Appendix: nomenclature

C	Tracer concentration in the liquid phase [M L^{-3}]
C_0	Tracer concentration in the injected solution [M L^{-3}]
C_{in}	Tracer concentration at the input [M L^{-3}]
C_{out}	Tracer concentration at the output [M L^{-3}]
D	Dispersion coefficient [$\text{L}^2 \text{T}^{-1}$]
D_{M}	Coefficient of diffusion molecular [$\text{L}^2 \text{T}^{-1}$]
i	Hydraulic gradient [L L^{-1}]
k	Hydraulic conductivity [L T^{-1}]
k_1	Irreversible sorption rate coefficient [$\text{L}^3 \text{M}^{-1} \text{T}^{-1}$]
k_2	First reversible sorption rate coefficient [$\text{L}^3 \text{M}^{-1} \text{T}^{-1}$]
k_3	Second reversible sorption rate coefficient [T^{-1}]
K_{H}	Henry distribution coefficient [$\text{L}^3 \text{M}^{-1}$]
K_{F}	Freundlich sorption coefficient [$\text{L}^3 \text{M}^{-1}$]
L	Column length [L]
n	Total porosity [–]
n_{e}	Effective porosity [–]
n_{F}	Freundlich sorption exponent [–]
s	Tracer concentration in the solid phase (total sorbed-phase concentration) [M M^{-1}]
s_{e}	Tracer concentration in the solid phase throughout equilibrium sorption [M M^{-1}]
s_{n}	Tracer concentration in the solid phase throughout non-equilibrium sorption [M M^{-1}]
t	Time [T]
t_1	Final moment at which $C(t_1) < 0.01 C_0$ at the output [T]
t_2	Initial moment at which $C(t_2) < 0.01 C_0$ at the output [T]
t_{in}	Time interval of the tracer injection, when $C(t) = C_0$ at the input [T]
t_{max}	Time of maximum tracer concentration at the output [T]
x	Distance [L]
α	Longitudinal dispersivity [L]

α_L	Langmuir constant [$L^3 M^{-1}$]
β_L	Total sorption capacity of the solid phase [$M M^{-1}$]
δD_b	Percentage deviation of descriptors [%]
$\delta \varepsilon$	Percentage deviation of relative tracer recovery [%]
$\delta \sigma$	Percentage deviation of spread of the breakthrough curve [%]
δt_{max}	Percentage deviation of time of maximum tracer concentration [%]
ε	Relative tracer recovery [%]
ρ_s	Density of the porous medium [$M L^{-3}$]
σ	Spread of the breakthrough curve [T]

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10040-021-02338-8>.

Funding The results presented in this study were obtained as part of a research project financed by the National Science Centre resources (Poland), allocated on the basis of decision number DEC-2011/01/B/ST10/02063.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- Ahmed MJ, Mohammed AHAK, Kadhum AAH (2011) Modeling of breakthrough curves for adsorption of propane, N-butane, and Isobutane mixture on 5A molecular sieve zeolite. *Transport Porous Media* 86(1):215–228. <https://doi.org/10.1007/s11242-010-9617-5>
- Arias M, Pérez-Novo C, Osorio F, López E, Soto B (2005) Adsorption and desorption of copper and zinc in the surface layer of acid soils. *J Colloid Interface Sci* 288(1):21–29. <https://doi.org/10.1016/j.jcis.2005.02.053>
- Appelo CAJ, Postma D (1999) *Geochemistry, groundwater and pollution*. Balkema, Leiden, The Netherlands
- Barrow NJ (1978) The description of phosphate adsorption curves. *J Soil Sci* 29(4):447–462. <https://doi.org/10.1111/j.1365-2389.1978.tb00794.x>
- Bear J, Cheng AH-D (2010) *Modeling groundwater flow and contaminant transport*. Springer, Lisse, The Netherlands, 834 pp. <https://doi.org/10.1007/978-1-4020-6682-5>
- Ciążła J, Siepak M, Wójtowicz P (2018) Tracking heavy metal contamination in a complex river-oxbow lake system: middle Odra Valley, Germany/Poland. *Sci Total Environ* 616–617:996–1006
- Dai Z, Wolfsberg A, Reimus P, Deng H, Kwicklis E, Ding M, Ware D, Ye M (2012) Identification of sorption processes and parameters for radionuclide transport in fractured rock. *J Hydrol* 414–415:220–230. <https://doi.org/10.1016/j.jhydrol.2011.10.035>
- Domenico PA, Schwartz FW (1998) *Physical and chemical hydrogeology*. Wiley, New York
- Dragon K (2006) Chemizm wód podziemnych wielkopolskiej doliny kopalnej w obszarze między Obrą a Wartą [Groundwater chemistry of a confined aquifer of the Wielkopolska buried valley aquifer between the Odra and the Warta rivers]. *Geologos* 8:1–107
- Dragon K, Kasztelan D, Górski J, Najman J (2016) Influence of subsurface drainage systems on nitrate pollution of water supply aquifer (Tursko well-field, Poland). *Environ Earth Sci* 75:100. <https://doi.org/10.1007/s12665-015-4910-9>
- Dubus IG, Brown CD, Beulke S (2003) Sensitivity analyses for four pesticide leaching models. *Pest Manag Sci* 59(9):962–982. <https://doi.org/10.1002/ps.723>
- Fetter CW (1999) *Contaminant hydrogeology*, 2nd edn. Prentice Hall, Upper Saddle River, NJ
- Fetter CW (2001) *Applied hydrogeology*. Prentice Hall, Upper Saddle River
- Fohmann G, Maloszewski P, Seiler KP (2001) Experimental determination of the copper & antimony mobility in calcareous and non-calcareous aquifer sediments in columns and 1-D reactive transport modelling. In: Seiler KP, Eds SW (eds) *New approaches to characterizing groundwater flow*. Balkema, Lisse, The Netherlands, pp 315–319
- Holtz R, Kovacs W (1981) *An introduction to geotechnical engineering*. Prentice-Hall, Upper Saddle River, NJ
- Johnson GR, Gupta K, Putz DK, Hu Q, Brusseu ML (2003) The effect of local-scale physical heterogeneity and nonlinear, rate-limited sorption/desorption on contaminant transport in porous media. *J Contam Hydrol* 64(1–2):35–58. [https://doi.org/10.1016/S0169-7722\(02\)00103-1](https://doi.org/10.1016/S0169-7722(02)00103-1)
- Kaczmarek M, Kazimierska-Drobny K (2007) Estimation-identification problem for diffusive transport in porous materials based on single reservoir test: results for silica hydrogel. *J Colloid Interface Sci* 311(1):262–275. <https://doi.org/10.1016/j.jcis.2007.02.054>
- Karathanasis AD (1999) Subsurface migration of copper and zinc mediated by soil colloids. *Soil Sci Soc Am J* 63(4):830–838. <https://doi.org/10.2136/sssaj1999.634830x>
- Khan AA, Muthukrishnan M, Guha BK (2010) Sorption and transport modeling of hexavalent chromium on soil media. *J Hazardous Mater* 174(1–3):444–454. <https://doi.org/10.1016/j.jhazmat.2009.09.073>
- Kleczkowski AS (1984) *Ochrona wód podziemnych* [Groundwater protection]. Wyd. Geologiczne, Warsaw, Poland
- Koeppenkaströpt D, De Cario EH (1993) Uptake of rare earth elements from solution by metal oxides. *Environ Sci Technol* 27(9):1796–1802
- Krogulec E, Zabłocki S (2015) Relationship between the environmental and hydrogeological elements characterizing groundwater-dependent ecosystems in central Poland. *Hydrogeol J* 23:1587–1602. <https://doi.org/10.1007/s10040-015-1273-y>
- Lichtner PC (1996) *Continuum formulation of multicomponent-multiphase reactive transport*. Center for Nuclear Waste Regulatory Analyses, San Antonio, TX, 87 pp
- Lichtner PC, Steefel CI, Oelkers EH (1996) *Reactive transport in porous media*. Mineralogical Society of America, Washington, DC
- Limousin G, Gaudet J-P, Charlet L, Szenknect S, Barthes V, Krimissa M (2007) Sorption isotherms: a review on physical bases, modeling and measurement. *Appl Geochem* 22:249–275. <https://doi.org/10.1016/j.apgeochem.2006.09.010>
- Lin G, Chen W, Liu P, Liu W (2019) Experimental study of water and salt migration in unsaturated loess. *Hydrogeol J* 27:171–182. <https://doi.org/10.1007/s10040-018-1861-8>
- Liu C, Zachara JM, Qafoku NP, Wang Z (2008) Scale-dependent desorption of uranium from contaminated subsurface sediments. *US Geol Surv Water Resour Res* 44(8):W08413
- Liu K-H, Enfield CG, Mravik SC (1991) Evaluation of sorption models in the simulation of naphthalene transport through saturated soils.

- Groundwater 29(5):685–692. <https://doi.org/10.1111/j.1745-6584.1991.tb00560.x>
- Liu D, Zhou J, Zhang W, Huan Y, Yu X, Li F, Chen X (2017) Column experiments to investigate transport of colloidal humic acid through porous media during managed aquifer recharge. *Hydrogeol J* 25:79–89. <https://doi.org/10.1007/s10040-016-1465-0>
- Luckner L, Schestakow WM (1991) Migration processes in the soil and groundwater zone. Lewis, Boca Raton, FL
- Małecki JJ, Nawalany M, Witczak S, Gruszczyński T (2006) Wyznaczanie parametrów migracji zanieczyszczeń w ośrodku porowatym dla potrzeb badań hydrogeologicznych i ochrony środowiska, Poradnik metodyczny [Determination of contaminant migration parameters in a porous medium for hydrogeological and environmental protection research: methodological guide]. UW Wydział Geologii, Warsaw, Poland
- Małecki JJ, Kadzikiewicz-Schoeneich M, Eckstein Y, Szostakiewicz-Hołownia M, Gruszczyński T (2017) Mobility of copper and zinc in near-surface groundwater as a function of the hypergenic zone lithology at the Kampinos National Park (central Poland). *Environ Earth Sci* 76:276. <https://doi.org/10.1007/s12665-017-6527-7>
- Maraqa MA (2007) Retardation of nonlinearly sorbed solutes in porous media. *J Environ Eng* 133(12):587–594. [https://doi.org/10.1061/\(ASCE\)0733-9372\(2007\)133:12\(1080\)](https://doi.org/10.1061/(ASCE)0733-9372(2007)133:12(1080))
- Maraqa MA, Khashan SA (2014) Modeling solute transport affected by heterogeneous sorption kinetics using single-rate nonequilibrium approaches. *J Contaminant Hydrol* 157:73–86. <https://doi.org/10.1016/j.jconhyd.2013.11.005>
- Marciniak M, Kaczmarek M, Okońska M, Kazimierska-Drobny K (2009) Identyfikacja parametrów hydrogeologicznych z zastosowaniem numerycznej symulacji krzywej przejścia oraz metod optymalizacyjnych [The identification of hydrogeological parameters on the basis of a numerical simulation of a breakthrough curve and optimization methods]. Bogucki Wyd, Naukowe, Poznań, Poland
- Okońska M, Kaczmarek M, Małoszewski P, Marciniak M (2017) The verification of the estimation of transport and sorption parameters in the MATLAB environment: a column test. *Geol Geophys Environ* 43(3):213–227. <https://doi.org/10.7494/geol.2017.43.3.213>
- Okońska M, Kaczmarek M, Marciniak M (2019a) The pulse descriptors in sensitivity studies of hybrid sorption column transport models. *J Porous Media* 22(6):647–662
- Okońska M, Marciniak M, Kaczmarek M (2019b) The pulse descriptors in sensitivity studies of no-sorption and single-sorption column transport models. *J Porous Media* 22(5):563–582
- Okońska M, Marciniak M, Zembrzuska J, Kaczmarek M (2019c) Laboratory investigations of diclofenac migration in saturated porous media: a case study. *Geologos* 25(3):213–223. <https://doi.org/10.2478/logos-2019-0023>
- Saiers JE, Hornberger GM (1996) Migration of ^{137}Cs through quartz sand: experimental results and modeling approaches. *J Contaminant Hydrol* 22:255–270
- Steeffel CI, Lichtner PC (1994) Diffusion and reaction in rock matrix bordering a hyperalkaline fluid-filled fracture. *Geochim Cosmochim Acta* 58:3595–3612. [https://doi.org/10.1016/0016-7037\(94\)90152-X](https://doi.org/10.1016/0016-7037(94)90152-X)
- Steeffel CI, DePaolo DJ, Lichtner PC (2005) Reactive transport modeling: an essential tool and a new research approach for the earth sciences. *Earth Planet Sci Lett* 240(3–4):539–558
- Van Genuchten M, Wierenga PJ (1976) Mass transfer studies in sorbing porous media: I. analytical solutions. *Soil Sci Soc Am J* 40(4):473–480
- Walna B, Siepak M (2012) Heavy metals: their pathway from the ground, groundwater and springs to Lake Góreckie (Poland). *Environ Monitor Assess* 184(5):3315–3340. <https://doi.org/10.1007/s10661-011-2191-7>
- Weber WJ Jr, McGinley PM, Katz LE (1991) Sorption phenomena in subsurface systems: concepts, models and effects on contaminant fate and transport. *Water Res* 25(5):499–528. [https://doi.org/10.1016/0043-1354\(91\)90125-A](https://doi.org/10.1016/0043-1354(91)90125-A)
- Wehrhan A, Kasteel R, Simunek J, Groeneweg J, Vereecken H (2007) Transport of sulfadiazine in soil columns: experiments and modeling approaches. *J Contaminant Hydrol* 89(1–2):107–135. <https://doi.org/10.1016/j.jconhyd.2006.08.002>
- Witczak S, Kania J, Kmiecik E (2013) Katalog wybranych fizycznych i chemicznych wskaźników zanieczyszczeń wód podziemnych i metod ich oznaczania [Guidebook on selected physical and chemical indicators of groundwater contamination and methods of their determination]. Inspekcja Ochrony Środowiska, Warsaw, Poland
- Yu C, Zhou M, Ma J, Cai X, Fang D (2019) Application of the homotopy analysis method to multispecies reactive transport equations with general initial conditions. *Hydrogeol J* 27(5):1779–1790. <https://doi.org/10.1007/s10040-019-01948-7>
- Zhu J (2019) Sensitivity of contaminant travel time to the combined effect of porosity and hydraulic conductivity. *Hydrogeol J* 27:615–623. <https://doi.org/10.1007/s10040-018-1881-4>

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.