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Assessment of the repeatability of column experiments results on the example of a conservative tracer

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Abstract

Most studies on the behavior of pollutants in the groundwater environment are carried out in laboratories, and the results are then implemented at local and regional levels using model simulations or analytical solutions. Column experiments are used to determine the transport characteristics of inorganic and organic chemicals in the soil and water environment. Although column experiments have been conducted regularly for many years, there is currently no established standard protocol for setting up and conducting them to ensure consistent results. The repeatability of column experiments was evaluated for soils, which differ primarily in the silt and clay content, using a conservative tracer susceptible only to advection and dispersion processes to reduce the number of variables affecting the results of the study which arise in a case of using reactive contaminants. The column experiments performed according to the adopted methodology are characterized by high repeatability of the obtained test results for the transport parameters, regardless of the type of injection or the chosen column length (only a small-scale effect is visible). Based on the results, it can be noticed that for the same soil the values of the pore–water velocity for different types of injections and column lengths are very similar. The percentage difference between the values of pore–water velocity obtained for both tested soils does not exceed 5% and for individual pairs of parallel column experiments it does not exceed 3%.

Keywords: transport parameters, sorption, repeatability, uncertainty, chloride ions, CXTFIT/STANMOD

1. Introduction

Nowadays, many pollutants from different sources enter the aquatic environment – groundwater and surface waters. Due to the complexity of natural systems and the wide range of factors affecting field-scale elimination processes, it is generally extremely rare to attribute specific effects observed in practice to a single, well-founded parameter. For this reason, the behavior of pollutants in the aquatic environment is usually tested on a laboratory scale, and the results obtained are used at the local and regional level by means of analytical solutions or model simulations. The determination of the transport parameters of inorganic and organic substances in the soil and water environment is carried out mostly using dynamic tests – column experiments. The experiments are carried out in an open system (column filled with soil), which allows the exchange of substances between the water solution and the soil environment. As a result, breakthrough curves of the conservative and reactive substances are obtained, which can be used to determine the transport parameters (e.g., pore-water velocity, dispersion coefficient, retardation factor, etc.) (Flores-Céspedes et al., 2002; Casey et al., 2005; Scheytt et al., 2006; Selim et al., 2010; Siemens et al., 2010; Leiva et al., 2017; Lehmann et al., 2018; Okońska et al., 2019; Pietrzak et al., 2019).

Although column experiments have been performed frequently for many years, there is still no standardized procedure to prepare and perform them in such a way that the results obtained are repeatable. This was noticed by, among others, Lewis & Sjöstrom (2010), who pointed out that "despite at least 300 years of experience in the use of soil columns, no standardization of experimental methods has occurred". Additionally, they emphasized that many experimental methods and approaches found in the literature are specific to individual researchers or research teams, which makes it challenging to directly compare results across various studies. This is largely necessary because different types of experiments often demand significantly different experimental approaches. Finally, they gave a review of the best practices associated with various types of soil column experiments (both saturated and unsaturated soil columns), to provide researchers with solutions to common design challenges, and contribute to better reproducibility in the experimental results obtained.

The same conclusions were also reached by Gibert et al. (2014), who conducted a review in the scientific literature of the practical aspects of design, operation, and monitoring of a column experiment for the simulation of a managed aquifer recharge (MAR), focusing on the behavior of emerging organic contaminants (EOCs). Based on the review they showed a guideline protocol for soil-column experiments assessing the fate and transport of trace organics. However, this protocol is oriented to simulate only case specific MAR system.

In 2016, Banzhaf & Hebig also pointed out that "although column experiments are frequently used to investigate the transport of organic micropollutants, little guidance is available on what they can be used for, how they should be set up, and how the experiments should be carried out". For this reason, they reviewed the use of column experiments to investigate the fate of organic micropollutants, showing alternative setups and discussing together with their respective advantages and limitations. Finally, they also offered suggestions on how to improve the comparability of future results from different experiments.

On the other hand, in the literature can be found a guideline for column experiment-related procedure – Leaching procedures for subsequent chemical and ecotoxicological testing of soil and soil-like materials – Part 3: Up-flow percolation test (PN-EN ISO 21268-3, 2020), and the use of this procedure to achieve repeatability and reproducibility of the tests (e.g., Yasutaka et al. (2017)). However, this norm is oriented only to the up-flow column percolation test for contaminated soil, which is not a standard form of conducting column experiments to investigate the transport of organic and inorganic pollutants.

All mentioned above paper pointed out the need for standardization of experimental methods for column experiments, which could not only facilitate comparisons between different experiments but also as pointed out by Banzhaf & Hebig (2016) could achieve a more universal understanding of the transport and fate of organic and inorganic pollutants in groundwater. It is not easy to achieve, because the setup used invariably depends very much on the specific research question being investigated. What is more, in most cases, individual experiments are performed to determine the transport parameters of the compounds tested. This carries the risk that mistakes are made at every stage of the research without the possibility of recognizing them. Errors made during the experiments influence the uncertainty of the final result.

According to the definition of the international organization established by the International Bureau of Weights and Measures (BIPM, 2024), measurement uncertainty is a "non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used". It is a "parameter, associated with the result of a measurement, that characterizes the dispersion of values that could reasonably be attributed to the thing being measured" (Ellison & Williams, 2012).

One of the most effective methods for estimating uncertainty in experimental results is to identify the main sources of uncertainty for individual phases of research and estimate their contribution to the overall balance of uncertainty (Williams & Magnusson, 2007; da Silva & Williams, 2015; Magnusson et al., 2017).

Several publications have attempted to analyze the factors influencing the results of column experiments or to assess the uncertainty of the determined parameters (Hebig et al., 2014; Kurwadkar et al., 2014; Banzhaf & Hebig, 2016; Ritschel & Totsche, 2016; Vitale et al., 2018). However, the sources and contribution of uncertainty arising in the different phases of the column experiments and their effects on the obtained values of the transport parameters have still not been clearly identified and recognized.

Measurement repeatability means – measurement precision under a set of repeatability conditions of measurement (the same measurement procedure, same operator, same measuring system, same operating conditions, and same location, and replicate measurements on the same or similar objects over a short time). In turn, the precision of measurement means – the closeness of agreement between indications or measured quantity values obtained by replicating measurements on the same or similar objects under specified conditions (Halligan, 2002; BIPM, 2024; NIST, 2024).

Responding to the need for standardization of experimental methods for column experiments, the study aimed to evaluate the repeatability of the results of column experiments using the example of a conservative tracer. The objective of the studies was to identify the main factors that – according to the authors – can significantly affect the uncertainty of the results of column experiments, and then experimentally verify how they can affect the repeatability of the research results. The main factors that were taken into account during studies were the dimensions of the columns, the method of soil packing and the method of tracer injection. To limit the number of factors influencing the research results, a conservative tracer (chloride ions – Cl^{-}), which is conservative in the tested terms and is only subject to advection and dispersion processes, was used to evaluate the repeatability of column experiments.

2. Column experiments and uncertainty of their results

The column experiments were planned and conducted according to the procedures described in the literature (Gibert et al., 2014; Banzhaf & Hebig, 2016). The diagram of the investigations carried out is shown in Fig. 1. A chloride solution with a suitable known concentration was added to a steel column filled with soil using a peristaltic pump (rate approx. 0.057 cm/min – which corresponds to the fast flow in the aquifer, approx. 300 m/year). Samples were taken from the outlet of the column at specific time intervals (every 14 minutes), which were then analyzed in the laboratory to determine the chloride concentration (using the titration method). The results were used to determine the breakthrough curves of the tracer (chloride) and their analysis in the STANMOD program enabled the determination of the transport parameters of the tested substance – pore–water velocity and dispersion coefficient.

Before planning the column experiments, the main factors potentially influencing the uncertainty of the results obtained were identified (Table 1) to take them into account in the experiments and at the same time minimize their impact on the research results. Not all these factors are directly applicable to column experiments for non–reactive substances, so the table also summarizes how they are taken into account when evaluating the repeatability of column experiments for a conservative trace.

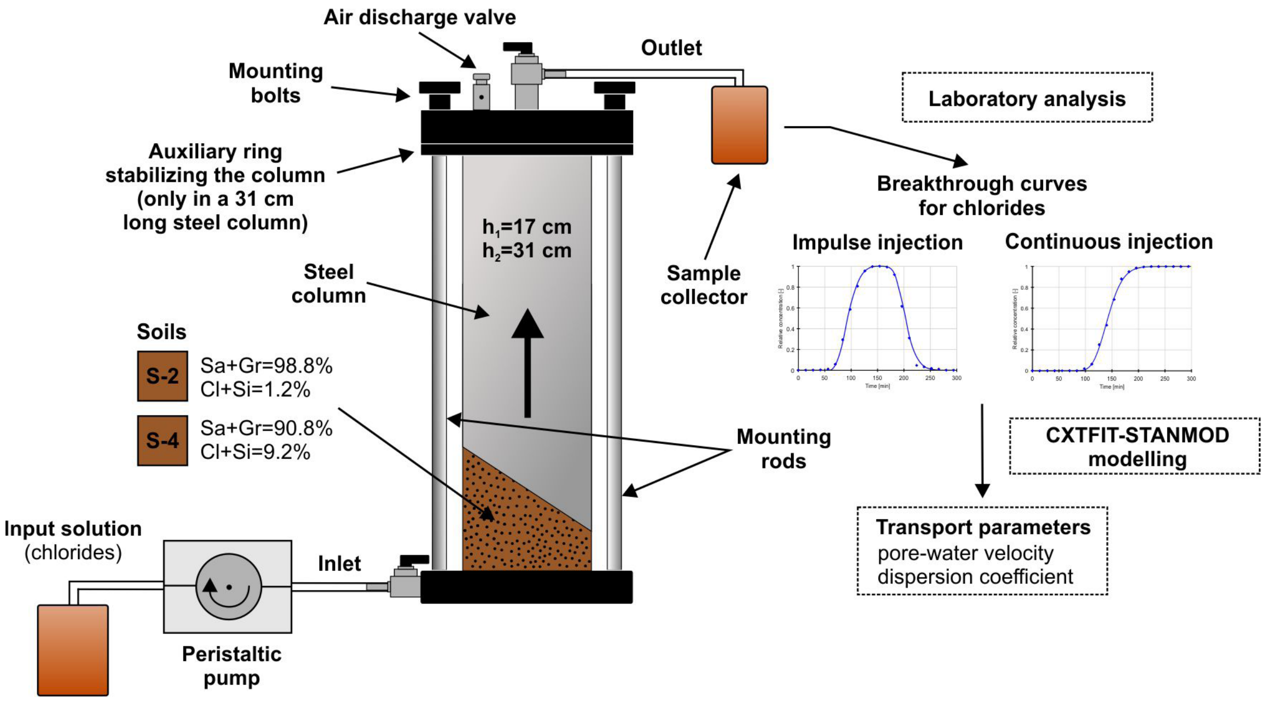


Fig. 1. Experimental setup and procedures for studying chloride transport parameters. Explanation: Sa – sand, Gr – gravel, Cl – clay, Si – silt.

Table 1. Main factors affecting the uncertainty of the results of column experiments.

Factors influencing the uncertainty of the result	Description and method of taking the factor into account in column experiments	A method of considering the factor in the assessment of repeatability in column experiments
	Preparation of the stand for experiments	
The material from which individual elements of the stand are made	Possibility of the tested compound reacting with this material (reactive substances – e.g., pesticides, pharmaceuticals, etc.). Reactivity assessment – experiments with deionized water and deionized water with the addition of the test substance – checking what percentage of the test substance can be absorbed on various materials of the stand.	Not applicable – conservative, non-reactive indicator
Column dimensions	Column dimensions influence the time that the tested substances stay in the column (soil). Various column sizes	Two identical test stands were built. Two column lengths were used: 17 and 31 cm, with a constant diameter of 6.4 cm (see section 3.1)
Preparation of soil samples	Ensuring the homogeneity of tested samples. A uniform procedure for preparing soil samples, e.g., using the cone and ring method to average the sample and the quartering method to reduce the sample (Campos & Campos, 2017; Mucha & Nieć, 2012).	A uniform procedure for preparing soil samples was used (see section 3.2)
	Laboratory experiments	
The method of packing the soil	The method affects the amount of material, the degree of its compaction and the possibility of creating zones of privileged flow. Various methods of soil packing, e.g., dry and wet packing, testing of the mass of soil filling the columns.	Tests were performed for 3 different soil packing methods to select the most optimal one (see section 3.3)
Solution for injection	Ensuring the uniformity and stability of the chemical composition. Uniform solution preparation methodology, laboratory stability tests.	A uniform methodology to prepare chloride solutions, and the compliance of its concentration with the concentration assumed for experiments was checked (see section 3.4)
Peristaltic pump rate	It forces flow through the soil at a specific filtration velocity, which affects the transport time of the tested substances in the soil. Peristaltic pump rate adjusted to the natural flow of groundwater in the tested aquifer.	The peristaltic pump rate used corresponds to the fast flow in the aquifer (approx. 300 m/year – see section 2)
Tracer type	Conservative or reactive tracer – considering the type of substance on the migration process in the soil (different values of transport parameters).	A conservative marker was used, subject only to advection and dispersion processes (see section 3.4)
Tracer injection method	Pulse and continuous injection — appropriate selection of concentration and experiment duration.	Two types of injection were used – continuous and pulse (see section 3.6)
Storage and transport of samples to the laboratory	The method of transporting samples and the time of their delivery to the laboratory may affect changes in the chemical composition of test samples. Transport in appropriate conditions and analysis of samples immediately after the experiment. See the standards ISO 5667 series.	Not applicable – the experiments were performed in a laboratory performing chloride analyses
Analytical methods	The test result is subject to uncertainty. Estimation of method uncertainty in the laboratory using standard procedures described, e.g., in da Silva & Williams (2015), Ellison & Williams (2012), Williams & Magnusson (2007).	The titration method was used, with uncertainty estimated by the laboratory (see section 3.4)

3. Methods

3.1. Construction of filtration columns

Two identical stands (1 and 2) were set up for the experiments using Humboldt permeability test kits, which were adapted to the specifics of the research conducted. Both stands were used in parallel. Each stand consisted of a base with an inlet valve and fixing rods, a stainless–steel column 17 cm long and 6.4 cm in diameter or 31 cm long and 6.4 cm in diameter and a cover equipped with an outlet valve and an air discharge valve (Fig. 1). The steel columns used had an irregular inner surface to minimize the possibility of creating privileged flow paths when the soil came into contact with the column surface. An additional element used to equip the station with a longer column was an auxiliary ring placed between the column and the cover. Its function was to stabilize the column while it was filled with soil and the cover was installed.

A Munktell type 388 paper filter was fitted above and below the column packing (at the base and on the column cover) to prevent clogging of the inlet and outlet valves. The final components of the system were silicone hoses, which supplied and discharged the solution into and out of the column.

3.2. Soil characteristics and its preparation

Two permeable natural soils were used in the column experiments, which differ in the content of the individual fractions. The use of natural soils was dictated by the attempt to simulate the transport of the component in a matrix as close as possible to the actual aquifer. The properties of the soils tested are listed in Table 2. More information on the methodology of sampling and preparation of soils for the column experiments can be found in the article (Pietrzak et al., 2022).

3.3. Method of soil packing

Before starting the column experiments, research was carried out on how to fill the column with soil. This stage aimed to compare the 3 most frequently used methods of preparing a column for an experiment:

– I – filling the column with dry soil (Leiva et al., 2017)
– II – filling the column with wet soil (Masipan et al., 2016),
– III – filling the column with dry soil and simultaneously irrigating it (Pietrzak et al., 2024).

Table 2. Characteristics of soils used in column experiments.

Soil properties	Soil S-2	Soil S-4
Textural name of the soil	medium sand	loamy sand
Gravel [%]	3.1	3.2
Sand [%]	95.7	87.6
Silt [%]	0.9	7.8
Clay [%]	0.3	1.4
Organic matter [g/kg]	0.021	0.13
pH	8.02	7.05
Cation exchange capacity [mval/100 g]	0.28	2.70

In the 'dry' method, the column was filled with dry soil in small portions and the soil was compacted mechanically (e.g., using a tamper). After filling the column, the soil was completely saturated with water, which was supplied from below by a peristaltic pump. In the 'wet' method, the column was filled with wet soil, which was also mechanically compacted in the meantime. In the third method, the test column was filled with dry soil in layers 1 to 2 cm thick, with distilled water being constantly added from below.

To investigate how the column can be filled with soil, two shorter columns with a length of 17 cm were used. Both columns were filled simultaneously with the same soil according to the chosen method. A total of six experiments were conducted, with each column preparation method being tested twice for each soil.

The total porosity of the soils that filled the columns was calculated based on the masses of dry and fully moist soils.

3.4. Laboratory analysis

Distilled water and an input solution containing a conservative tracer in the form of chloride were used in the column experiments. Deionized water was used to saturate the soils while the column was packed in the preparation phase and was used as a solution with a tracer concentration of zero during the experiment.

The input solution was prepared in the laboratory by dissolving pure sodium chloride in solid form in deionized water. After preparation, the solution was stored in a tightly sealed volumetric flask. The chloride concentration in the input solution was 300 mg/L. Each time after the preparation of the input solution, its concentration was checked to match the concentration assumed for the experiments and the stability of this composition was checked during the experiments.

The concentration of chloride ions in the input solution and the output solution in the samples taken during the experiment was determined using the titration method. The tests were carried out in the KHGI Hydrogeochemical Laboratory (PCA accreditation certificate no. AB 1050) following the PN-ISO 9297:1994 standard. The uncertainty of the chloride determination stated by the laboratory during the method verification was 4.9%. This is the expanded uncertainty with the expansion factor uncertainty = 2 at the 95% confidence level.

3.5. Data processing

To process data from column experiments, the CXTFIT/STANMOD software package was used, which includes a modified and updated version of the CXTFIT code for estimating tracer transport parameters using a nonlinear least squares method for parameter optimization (Parker & Vangenuchten, 1984; Toride, 1995).

The CXTFIT/STANMOD software assumes (according to the theory of column experiments) that the flow of substances dissolved in water in porous media occurs as a result of the combined effects of convection and dispersion – the convection-dispersion equation (CDE). Assuming steady-state flow, linear adsorption, first-order decay and zero-order production, the one-dimensional CDE model can be described by the following equation (Toride, 1995; Simunek et al., 1999):

$$R\frac{\delta C_s}{\delta t} = D\frac{\delta^2 C_s}{\delta x^2} - U\frac{\delta C_s}{\delta x} - \mu C_s + \gamma(x)$$

where:
C_s – concentration of the solute in the liquid phase [mg/L],
t – time [h],
D – dispersion coefficient [cm^2/h],
x – spatial coordinate in the flow direction [cm],
U – pore–water velocity [cm/h],
μ – decay constant for first-order reaction kinetics [1/h],
γ – zero-order production value [mg/L/h],
R – retardation factor [-].

The CXTFIT–STANMOD software was used to determine transport parameters based on the breakthrough curves and the above deterministic equilibrium CDE equation (Model type – *Deterministic equilibrium* CDE), solving the inverse problem. Based on the input data (location – at the outlet from the column, sample collection time, and chloride concentration in the collected samples) and initially estimated parameters, the pore-velocity of water with chloride (U) and the dispersion coefficient (D) were calculated, adjusting one of the analytical solutions to the given experimental data.

3.6. Experimental scheme of repeatability assessment of column experiments

The experiments were performed under repeatability conditions – same measurement procedure, same operator, same measurement system, same operating conditions and location, and repeated measurements on the same objects within a short period. The factors (from Table 1) that changed during the experiments were:
- type of soil – two types of well–permeable soil (Table 2);
- method of packing the soil in a column – three methods described in Section 4.1;
- type of injection – continuous and pulse;
- column length – 17 and 31 cm.

Column experiments were performed using two types of injections – continuous and pulse – for two lengths (17 and 31 cm) of the migration paths. The experimental results were then used to estimate the transport parameters using the CXTFIT–STANMOD package. The repeatability of the column experiments was then checked based on the determined transport parameters (pore–water velocity and dispersion coefficient).

4. Results

4.1. Ways to fill the column with soil

The result of the first research phase was a comparison and the choice of one of the three methods for filling the column with soil for further experiments (Table 3).

Examination of how the column is filled with soil showed that the results for each method achieved a similar degree of repeatability. The maximum difference in the mass of soil used between the columns for a given method is 16.6 g (medium sand, method II), which is less than 1.8% of the mass difference. In addition, it can be noted that the highest mass of soil filling the column, and thus the lowest porosity was obtained using Method I, both for medium sand (S-2) and loamy sand (S-4). For the other

Table 3. Values of parameters related to soil packing for each of the tested methods of preparing the column for the experiment.

Method of filling the column with soil		Method I		Method II		Method III	
Stand		1	2	1	2	1	2
Soil S-2	Mass of soil in the column [g]	951.7	951.0	921.5	904.9	935.1	935.2
	Weight difference [%]	0.07		1.80		0.01	
	Total porosity [-]	0.34	0.34	0.36	0.38	0.35	0.35
Soil S-4	Mass of soil in the column [g]	957.0	946.1	943.0	941.8	933.2	931.6
	Weight difference [%]	1.14		0.12		0.17	
	Total porosity [-]	0.34	0.35	0.35	0.35	0.36	0.36

methods, the situation varied depending on the soil – for S-2 the lowest mass of soil filling the column and the highest porosity was achieved using Method II and for soil S-4 using Method III.

In this phase, the advantages and disadvantages of the individual column filling methods were determined. The main disadvantage of Method I, in which the column was filled with dry soil, was that the mechanical compaction of the soil caused larger and heavier grains to move to the bottom of the column. This process can lead to the formation of zones with different grain sizes and privileged flow paths in the column, which significantly impairs the repeatability of the test. In Method II, where the column was filled with wet soil, there was no problem with the sorting of the soil particles, but another problem appeared related to estimating the appropriate amount of water required to previously moisten the soil. The dry part of the soil was able to absorb significant amounts of water during saturation beyond the typical soil moisture content. The high-water content led to a slight plasticization of the soil during mechanical compaction. This was particularly problematic in the case of soil S-4, which contains a higher proportion of silt and clay. This method did not guarantee complete displacement of the air from the pore space of the soil. These shortcomings were eliminated using Method III. The constant flow of distilled water from the bottom of the column allowed the natural compaction of the soil without sorting the grains by size and weight and the displacement of air from the pore space. This method also avoided the problem of excessive plasticization of the soil during compaction caused by an incorrect choice of the amount of water required for irrigation. The disadvantage of method III is the risk of achieving a lower degree of soil compaction than with the two methods described above.

When selecting the method for filling the column with soil, the criterion of repeatability was primarily taken into account. For both soils, Method III gave the most similar values for the soil mass filling the column and the porosity. In addition, this method limited the possibility of problems that occurred with the previous two methods, i.e. the formation of zones of preferential flow paths, limited the possibility of soil plasticization and allowed the displacement of air from the pore space. Taking the above into account, Method III was used to fill the column with soil for further column experiments.

4.2. Pulse injection – 17 cm long column

For each type of injection and column length, two tests were performed simultaneously (marked stand 1 and stand 2). For all experiments using pulse injections, the injection duration was 110 min.

For the S-2 soil, the test duration was 270 minutes and 17 samples of the chloride solution were taken from each column during the test. A rapid increase in chloride concentration was observed in both columns, which then remained at a level corresponding to the concentration of the input solution for 56 minutes. The curves obtained have a symmetrical shape (Fig. 2A).

The estimated pore–water velocity was 0.182 cm/min for stand 1 and 0.185 cm/min for the second one, respectively (Table 4). The values of the dispersion coefficient were similar and amounted to 0.052 cm^2/min for stand 1 and 0.051 cm^2/min for stand 2, respectively.

In the case of soil S-4, the test duration was longer (340 minutes) and 22 samples of the chloride solution were taken from each column during the test. In both stands, the highest recorded concentration of the output solution did not reach the concentration of the input solution. The peak of the breakthrough curve was reached at minute 154 of the experiment in both stands. In addition, the breakthrough curves obtained had a right-asymmetric shape (Fig. 2B).

The determined pore–water velocity of the chloride is the same for both stands and amounts to 0.158 cm/min. The values of the dispersion coefficient are similar and amount to 0.257 cm^2/min for stand 1 and 0.243 cm^2/min for stand 2 (Table 4).

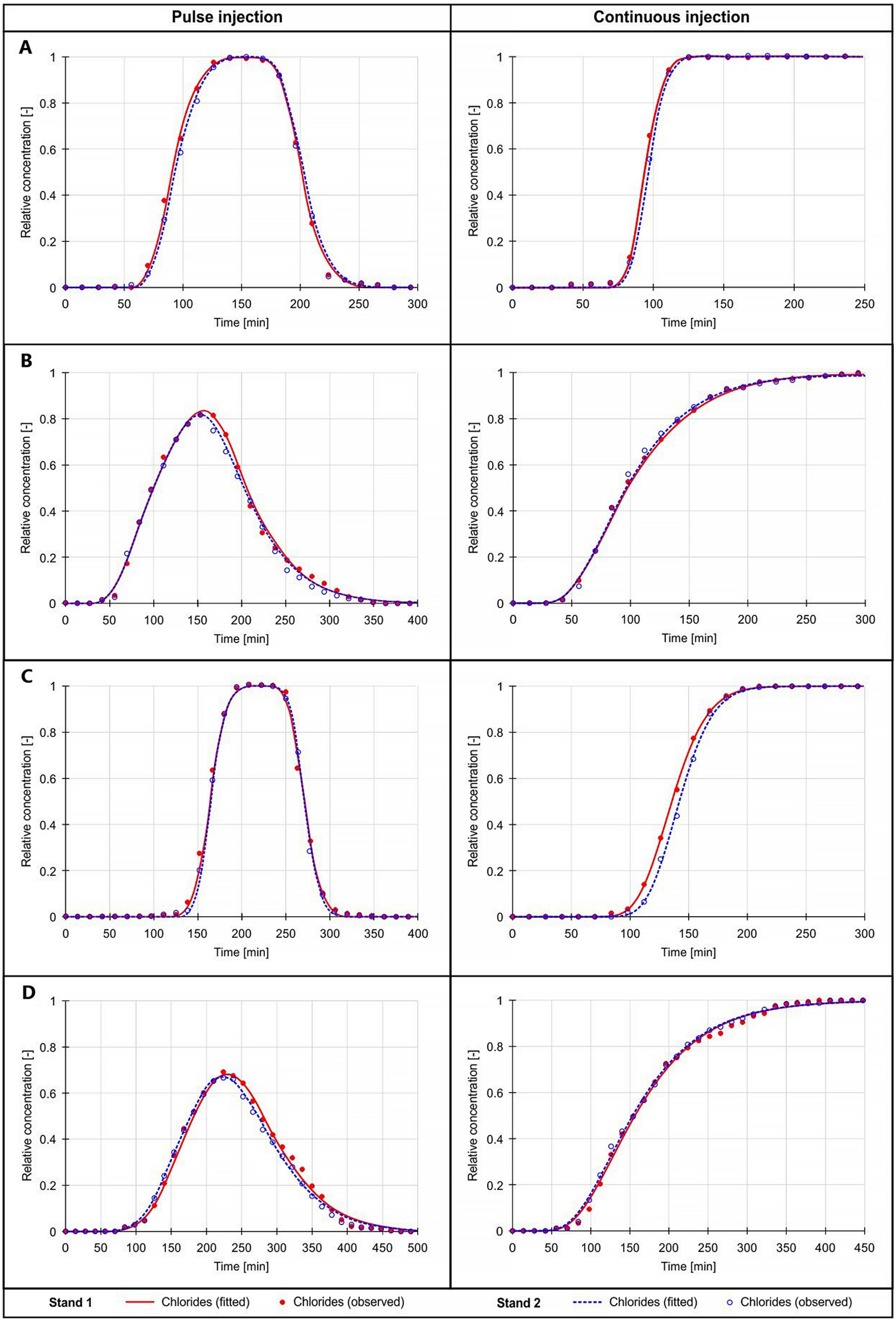


Fig. 2. Chloride breakthrough curves through 17 cm long columns for soil S-2 **(A)** and S-4 **(B)** and through 31 cm long columns for soil S-2 **(C)** and S-4 **(D)** during pulse and continuous injection.

Table 4. Reproducibility of the results of column experiments for different column lengths and injection types. Explanation: R^2 – determination coefficient [-].

Stage	Soil	Stand	Pore–water velocity [cm/min]	Dispersion coefficient [cm²/min]	R^2 [-]
Column length 17 cm Pulse injection	S-2	1	0.182	0.052	0.996
		2	0.185	0.051	0.997
	S-4	1	0.158	0.257	0.995
		2	0.158	0.243	0.994
Column length 31 cm Pulse injection	S-2	1	0.187	0.077	0.999
		2	0.186	0.063	0.998
	S-4	1	0.158	0.310	0.994
		2	0.158	0.294	0.993
Column length 17 cm Continuous injection	S-2	1	0.178	0.017	0.999
		2	0.179	0.017	0.999
	S-4	1	0.163	0.281	0.996
		2	0.158	0.302	0.998
Column length 31 cm Continuous injection	S-2	1	0.182	0.070	0.999
		2	0.181	0.059	0.999
	S-4	1	0.160	0.364	0.998
		2	0.160	0.352	0.999

4.3. Pulse injection – 31 cm long column

The experiment for soil S-2 lasted 340 minutes and 17 samples of the chloride solution were taken from each column during the test. The indicated breakthrough curves were characterized by a symmetrical shape. The concentration of the output solution reached the concentration of the input solution after 196 minutes. The resulting peak of the breakthrough curve persisted in both stands for 70 minutes (Fig. 2C).

The estimated transport parameters are similar in both stands. The pore–water velocity was 0.187 cm/min for the first stand and 0.186 cm/min for the second stand. The dispersion coefficients are 0.077 cm²/min and 0.063 cm²/min, respectively (Table 4).

In turn, the experiment for soil S-4 lasted 440 minutes, during which 27 samples of chloride solution were taken from each column. The breakthrough curves obtained assumed an analogous, right-asymmetric shape as in the case of the experiment with shorter columns. In this study, the maximum concentration of the output solution reached about 0.65 of the concentration of the input solution. The peak of the breakthrough curve occurred in both stands 224 minutes after the start of the experiment (Fig. 2D).

The determined pore–water velocity was the same for both stands and amounted to 0.158 cm/min. The values of the dispersion coefficient were similar and amounted to 0.310 cm²/min for stand 1 and 0.294 cm²/min for stand 2, respectively (Table 4).

4.4. Continuous injection – 17 cm long column

The test duration for soil S-2 was 250 minutes. During the test, 16 samples of the chloride solution were taken from each column. According to the method used, the solution was injected throughout the experiment. The concentration of the output solution already corresponded to the concentration of the input solution in the 126th minute of the experiment (Fig. 2A).

The pore–water velocities determined were similar and amounted to 0.178 and 0.179 cm/min. The value of the dispersion coefficient in both stands was the same, equal to 0.017 cm²/min (Table 4).

The duration of the experiment for soil S-4 was longer and lasted 300 minutes. During this time, 16 samples of the solution were taken at the outlet of the column. The concentration of the solution at the column outlet reached a concentration close to that of the input solution and began to stabilize at the end of the experiment at 224 minutes (Fig. 2B).

The determined pore–water velocity was 0.163 and 0.158 cm/min, and the dispersion coefficients were 0.281 and 0.302 cm²/min for stand 1 and stand 2, respectively (Table 4).

4.5. Continuous injection – 31 cm long column

In the case of soil S-2, the concentration of the output solution was already equal to the concentration of the input solution in the 210th minute of the test (Fig. 2C), so the experiment duration was 300 minutes. During this time, 21 samples of the solution were taken from the outlet of the column.

The pore–water velocities determined were similar and amounted to 0.182 and 0.181 cm/min. The value of the dispersion coefficient in both stands also had similar values of 0.070 and 0.059 cm^2/min for stand 1 and stand 2, respectively (Table 4).

For soil S-4, the duration of the experiment was 450 minutes and 32 samples of the chloride solution were taken from each column. The concentration of the solution at the outlet of the column only reached a concentration close to that of the input solution after 390 minutes (Fig. 2D).

The determined pore-water velocity was the same for both stands and amounted to 0.160 cm/min, and the dispersion coefficients were 0.460 and 0.560 cm2/min for the first and second stands, respectively (Table 4).

5. Discussion

As a conservative tracer was used in the column experiments, the components of the transport equation (section 3.5) relating to sorption (retardation factor R=1), degradation (none) and production (none) were omitted. The remaining two components of the equation were considered – the pore–water velocity (U) and the dispersion (expressed by the dispersion coefficient – D).

Based on the column experiments results, it can be noticed that the values of the pore–water velocity for different types of injections and column lengths are very similar and are 0.178–0.187 cm/min for S-2 soil and 0.158–0.163 cm/min for soil S-4 (Fig. 3A). The percentage difference between the obtained values of pore–water velocity is not more than 5%. What is more, very similar values of the pore–water velocity for individual pairs of parallel column experiments were observed. The largest difference in the obtained test results for this parameter was observed for soil S-4 with continuous injection and a 17 cm long column, but this difference does not exceed 3%. Also, the values of the dispersion coefficient for both soils are very similar for individual pairs of parallel column experiments (Fig. 3B).

When considering hydrodynamic dispersion, it is important that it increases with the increase in the distance over which migration is considered (scale problem) (Marciniak et al., 2006). This phenomenon results from the presence of macro inhomogeneities with different soil properties in the aquifer. Hence, the values of the dispersion coefficient for individual soils differ depending on the length of the column – lower values for a column of 17 cm and higher values for a column of 31 cm. This regularity is observed regardless of the soil and the type of injection. A greater scale effect is observed for soil S-4, which is more heterogeneous than soil S-2. The dispersion coefficient ranges from 0.020-0.077 cm^2/min for S-2 soil, and from 0.24–0.36 cm^2/min for S-4. It is worth noting here that the scale effect is visible even on a laboratory scale – the column lengths differed only two times, which resulted in an increase in the dispersion coefficient value in the case of a longer column.

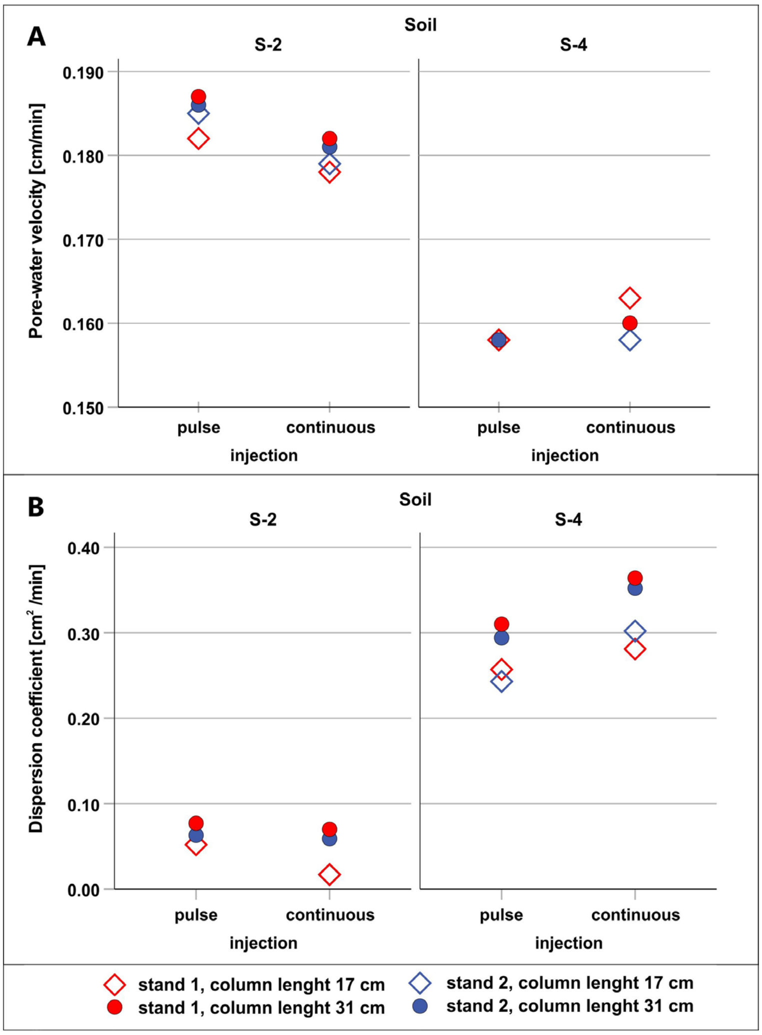
The repeatability of the results of column experiments is observed for both soils used in the study, which differ mainly in the content of the silt and clay fractions. This means that in this case the type of soil has no influence on the repeatability of the experiments and the method itself can be successfully used to study the transport of conservative and reactive pollutants using different soils.

On this basis, it can be concluded that the proposed methodology for performing column experiments is characterized by high repeatability of the obtained test results, regardless of the type of injection or column length adopted.

Since the main factors influencing the uncertainty of the obtained results were identified before planning the column experiments and taken into account in the experiments, it was possible to minimize their impact on the research results, which helped to demonstrate the repeatability of the method. The observed slight differences in the obtained experimental results result primarily from factors such as the heterogeneity of the soil, the heterogeneity of the prepared solutions, the uncertainty of the laboratory analyzes as well as the accuracy of the model fit to the measurement results of the real values in the CXTFIT–STANMOD software.

Based on the above conclusions, an attempt can be made to optimize the methodology for conducting column experiments. Since the proposed methodology is characterized by high repeatability of the obtained test results, regardless of the type of injection used or the length of the columns, a shorter column of 17 cm and a pulse injection can be successfully used for further investigations, which was examined for conservative tracer. Assuming that the time of transport of reactive tracers through the soil column is longer, it can be assumed that, also

Fig. 3. Values of pore–water velocity **(A)** and dispersion coefficient **(B)** for different experimental variants.



in the case of these reactive substances, the results will be repeatable. This will help to shorten the duration of the experiments and consequently reduce the number of leachate samples subjected to laboratory analysis. This in turn can help to reduce the cost of conducting column experiments, the majority of which is the cost of analyzing the compounds tested.

Many researchers employ a similar methodology for conducting column experiments, utilizing comparable column dimensions, flow rates, natural soils, and methods of packing the column, as well as CXTFIT/STANMOD software. They achieve high fits of experimental data to model data for conservative tracer in the range from 0.91 to 0.99 (Peña et al., 2011; Schaffer et al., 2015; Leiva, 2017; Rodríguez-Liébana et al., 2018; Sieczka & Koda, 2018; Liu et al., 2019; Kiecak et al., 2020). Also, when examining different column dimensions, researchers pay attention to the scale effect, especially in the case of the dispersion coefficient (Marciniak et al., 2006). However, these are usually single experiments, making it difficult to conclude the repeatability of the adopted research methodology. No similar studies have been found so far that would approach each stage of performing column experiments so comprehensively, with particular emphasis on the repeatability of the methodology and thus the obtained results of transport parameters.

6. Summary

Responding to the need for standardization of experimental methods for column experiments, an evaluation of the repeatability of the results of column experiments using the example of a conservative tracer was made. First, the main factors that – according to the authors – can significantly affect the uncertainty of the results of column experiments were identified, and those that can affect the repeatability of the research results were experimentally verified. These factors were primarily the dimensions of the columns, the method of soil packing and the method of tracer injection. In addition, to limit the number of factors affecting the research results, a conservative tracer (chloride) was used to evaluate the repeatability of the column experiments, subject only to advection and dispersion processes.

The column experiments performed according to the adopted methodology are characterized by a high repeatability of the obtained test results for the transport parameters (pore–water velocity and dispersion coefficient), regardless of the type of injection or the chosen column length. The percentage difference between the values of pore–water velocity obtained for both tested soils (S-2 and S-4) does not exceed 5% and for individual pairs of parallel column experiments it does not exceed 3%. Based on the research results, attempts can be made to optimize the methodology for conducting column experiments, primarily to reduce the time and cost of conducting the experiments.

When selecting the method for filling the column with soil, it is recommended to fill the column with dry soil and simultaneously irrigate it, which gives the most similar values for the soil mass filling the column and the porosity. This method also limited the possibility of the formation of zones of preferential flow paths, the possibility of soil plasticization, and allowed the displacement of air from the pore space.

The next stage of the research could be a comparison of the current test results on a laboratory scale (soil column length from a dozen to several dozen cm) with tests carried out in the same scale (laboratory test) or larger scale (field conditions), for example using lysimeters, reflecting the flow in the unsaturated zone. This could, in addition to assessing the impact of medium anisotropy on the transport rate of substances in the soil–water environment, confirm the scale effect already observed on the laboratory scale (with different column lengths) in relation to the dispersion coefficient values.

Correct determination of substance pore-water velocity on a laboratory scale, while maintaining the repeatability criterion, is important because these parameters constitute the basis for modeling the transport of substances on a regional scale. However, the dispersion coefficient depends strongly on the scale of the research; therefore, it cannot be used in regional models.

Finally, within the context of the absence of an accepted protocol or guidelines for performing column experiments, the paper aims to bring back the attention of the research community to agree on specific standards of, e.g., setup for column experiments or reference compounds and substrates to use in column experiments. This standardization would help to overcome the issue of comparability of results and make them transferable between different column experiments.

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Data availability

Data sets generated during the current study are available from the corresponding author on reasonable request.

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