Solute transport by groundwater – a comparison of computation methods sensitivity to physical-chemical parameters and source geometry

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Abstract: The presented comparative study evaluates the sensitivity of selected computational procedures to chosen parameters of solute transport and source geometry in homogeneous conditions. The computation procedures include three numerical schemes with FDI (finite difference implicit), MOC (method of characteristics), and a TVD (total variation diminishing) advection solver, while the other terms of the governing equation are computed by the FDI method. Furthermore, two analytical solutions were used: the exact solution of Newille (2005) and the approximate solution of Domenico (1987). Finally, a simplified, so-called Step-method, which is still being used in the practice, was used. The sensitivities of the individual procedures to selected physical-chemical parameters and to the geometric characteristics of the solute source were evaluated and compared. The obtained results show considerable differences between the particular procedures used. In most test cases, the numerical procedures with a TVD and MOC advection solver produced higher concentrations and were more sensitive to the transport parameters in comparison with the other methods used. Applied variations of individual parameter values caused a change of the calculated solute concentrations up to 7.1 %, whereas the substitution of calculation methods caused up to 7.7 % of C_0 (the concentration in solute source). The simultaneous changes of all the examined parameter values with a synergistic effect caused the maximal change of calculated concentration up to 15.3 % of C_0. A significant effect of the solute source geometry on the match between the results obtained by the selected numerical and analytical methods was also found (difference up to 57.9 % of C_0). The achieved results indicate a need to solve the solute transport in homogeneous conditions using both types of calculation methods, the numerical and analytical, in order to cover possible variability of resulting concentrations. The simplified Step-method predominantly yields the lowest concentrations. At the same time, it is the least sensitive procedure to the selected parameters and can be used only for a reference point situated on the plume centerline. From a cautious point of view, it is the least suitable method for solute transport modelling among the compared methods.
Key words: solute transport, analytical model, numerical model, transport parameters, method sensitivity

1. INTRODUCTION

Modelling of the dissolved substance transport by groundwater is one of the basic supporting tools of decision-making processes within the protection of groundwater and the environment. The objective of modelling is to predict solute concentrations in space and time. The process of solute transport is typically described by a partial differential equation, including the processes of advection, dispersion, sorption, and chemical reactions of the dissolved substance. This equation has both analytical and numerical solutions. In addition, the application of simplified Step-method according to the Ministry of the Environment of the Slovak republic guideline no 1/2015-7 (MoE SR, 2015) is accepted by authorities in Slovak Republic.

Analytical models are more economical and convenient in application as compared to numerical procedures. They also provide a simple and effective means for gaining insight into the relative importance of various transport parameters (Huyakorn et al. 1987). There are many specific analytical solutions that are suitable for a particular spatial and temporal configuration of the model domain, solute source, and reference points at which the

concentration of the dissolved substance is calculated. These are: 1D, 2D, 3D solutions for various types of solute sources and transport scenarios, as can be seen in the works of Ogata & Banks (1961), Ogata (1970), Bear (1972), Van Genuchten (1977), Huyakorn et al. (1987), Leij et al. (1991), Wexler (1992), Batu (1996), Newell et al. (1996), Guyonnet & Newille (2004), Newille (2005), Batu (2006), Srinivasan et al. (2007), West et al. (2007), Bear & Cheng (2010), Estabragh et al. (2013), Szucs et al. (2013), Singh et al. (2016), Pophillat et al. (2018), Antelmi et al. (2020) and others.

Numerical methods are based on discretization of space and time; therefore, they are suitable for inhomogeneous, complex conditions, and almost any spatial and temporal system configuration. However, their outcomes are subject to mass balance error, truncation error, numerical dispersion error, and artificial oscillation error (Harbaugh, 2005; Zheng & Wang, 1999). These errors can be kept at acceptable levels by using suitable procedures for particular conditions, as well as by thorough model settings. The accuracy of numerical schemes is often inspected by a comparison of their results with the results of exact analytical methods within homogeneous conditions. Description of

numerical schemes, their application, or verification by comparison with analytical solutions can be seen in the works of Molenkamp (1968), Bear (1972), Van Genuchten (1977), Bear & Verruijt (1987), Leij et al. (1991), Zheng & Wang (1999), Harbaugh (2005), Batu (2006), Bear & Cheng (2010), Estabragh et al. (2013), Szucs et al. (2013), Singh et al. (2016), Antelmi et al. (2020) and others. Nowadays, numerical models are often used for heat transport modelling as well, as can be seen in the works of Mendéz (2008), Pophillat et al. (2018), Krčmář et al. (2020) and others.

The aim of the study is to demonstrate how variation of transport parameter values, solute source dimensions, and exchange of computation schemes can affect the resulting solute concentration at a defined reference point. This objective is ensured by comparison of the solute concentrations, which are computed at selected reference points by means of selected computation methods, as well as by comparison of the sensitivity of particular methods to the selected input parameters and to the solute source geometry.

We hypothesize that there does exist a strong correlation between the results computed by numerical and analytical procedures; however, there is a weaker correlation between the results of the Step-method and the other methods used. We also expect some degree of discrepancy in the results between the exact ATRANS analytical solution of Newille (2005) and the approximate analytical solution of Domenico (1987), depending on the simulated conditions based on the findings of Guyonnet & Newille (2004), Srinivasan et al. (2007), and West et al. (2007).

2. METHODS

The chosen computation procedures include three numerical schemes with an FDI (finite difference implicit), MOC (method of characteristics), and TVD (total variation diminishing) advection solver, while the other transport equation terms are computed by the FDI method (Zheng & Wang, 1999), two analytical solutions (Newille, 2005; Domenico, 1987), and a simplified so-called Step-method (MoE SR, 2015).

The numerical 3D model of groundwater flow MODFLOW 2005 (Harbaugh, 2005) in connection with the numerical 3D solute transport model MT3DMS (Zheng & Wang, 1999) are used for all numerical calculations. Groundwater flow numerical simulations are applied by a "Layer property Flow" package with a "Preconditioned Conjugate Gradient" solver (Harbaugh, 2005).

All the numerical solute advection computations are performed with a central-in-space weighting scheme. Implicit numerical schemes of MT3DMS software are solved by a "Generalized Conjugate Gradient" solver with a "Modified Incomplete Cholesky preconditioner" (Zheng & Wang, 1999). Within the MOC procedure, the "Runge-Kutta only near sinks/sources" particle tracking algorithm is applied.

The software BIOSCREEN (Newell et al., 1996) is used for Domenico's approximate analytical model, and the software ATRANS (Newille, 2005) is used for Newille's exact analytical model of the same name.

The Step-method is applied in accordance with the solution

procedure specified in the Directive (MoE SR, 2015) for the elaboration of a risk analysis of contaminated site.

The applied analytical and numerical methods are defined as three - dimensional solutions of the solute transport equation in terms of modelled physical-chemical processes. However, with respect to the source and aquifer geometry, as well as the reference point localization, only the numerical methods are fully three-dimensional. The ATRANS analytical method applied within the eponymous software and Domenico's solution within the BIOSCREEN software are three-dimensional with respect to the modelled processes; they are two-dimensional with respect to the possibility of solute source representation. 3D localization of reference points is possible in all the numerical models including the ATRANS analytical model, while it is 2D within the BIOSCREEN model and 1D (on plume centerline) within the Step-method.

The Step-method does not represent a solution of a transport differential equation. It is a schematic, simplified 2D solution of the given processes with only vertical dispersion applied. All the above-mentioned limitations are considered a part of the application and evaluation of each method's results.

2.1. Conceptual model

The calculations are performed under simple conditions, i.e. the semi-infinite, rectangular model domain with finite thickness; steady, uniform, one-dimensional groundwater flow; homogeneous, porous aquifer; steady boundary conditions of Dirichlet type. In the case of numerical simulation, the solute source body has dimensions of 5 m, 100 m and 0.5 m in the respective directions x, y, z (Fig. 1). In the case of analytical models, the solute source is represented as a 2D partially penetrating patch, perpendicular to the groundwater flow with dimensions of 100 m and 0.5 m in the respective directions y, z. Within the Step-method, it is a partially penetrating 2D strip source, with a length of 0.5 m in the z direction. In all the test cases, the solute source has a constant concentration, uniform in all directions. It is situated in the middle of the upgradient side (Fig.1). These conditions are acceptable for all computation schemes used.

The horizontal dimensions of the presented model area are 500 m x 1,000 m. The aquifer thickness of 15 m is divided into 30 layers to perform the numerical solutions (Fig. 1). The groundwater head gradient of 0.002 is fixed in the numerical models by the constant head boundary condition. In the analytical models and the Step-method, the value of the groundwater head gradient is included directly into the calculation of the average porous velocity of groundwater flow.

In the basic setup of the numerical and analytical procedures, the width of the solute source is 100 m and the depth of penetration is 0.5 m below the groundwater surface (Fig. 1). The source dimensions were subsequently varied to examine its impact to the simulation results. The transport time is 1,000 days in all the simulations. This value allows for achieving a steady state (maximal attainable) concentration throughout the entire model domain.

The dimensions x, y, z of the calculation grid cells within all numerical simulations are 5 m, 5 m, and 0.5 m respectively for
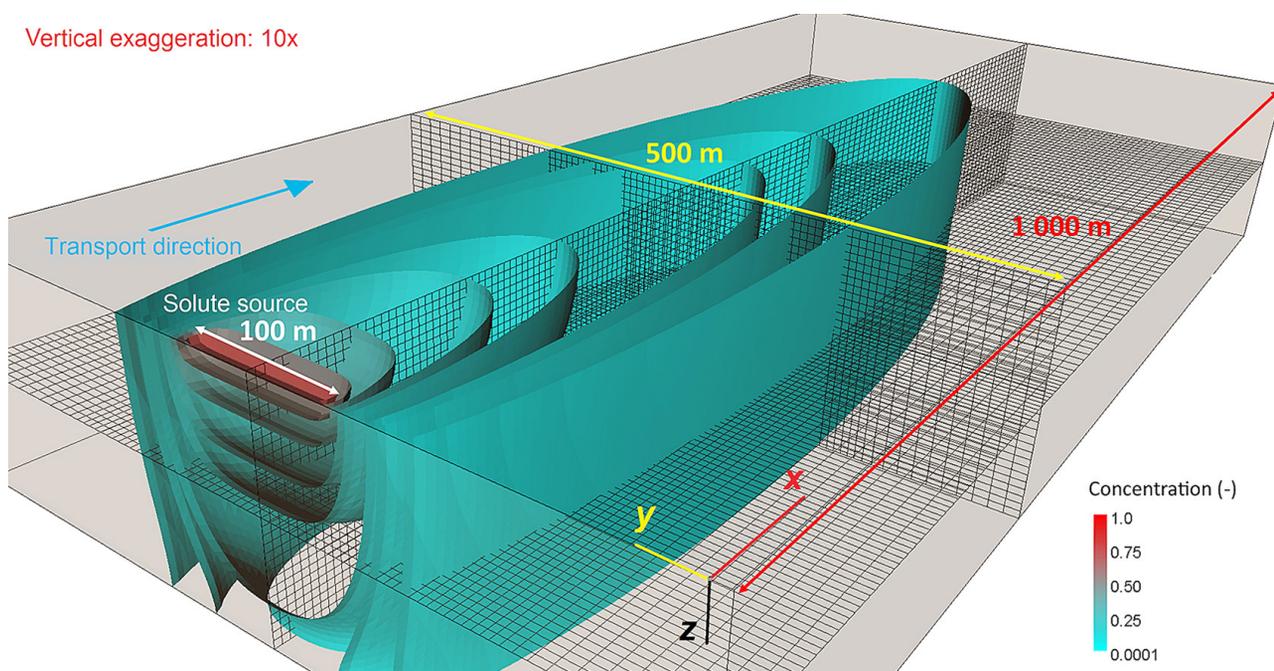
Fig. 1. Transport model domain with displayed basic dimensions, numerical grid, and concentration isosurfaces of the transported solute with its dimensionless concentrations.

the first 300 m of the transport along the longitudinal direction, and up to 100 m in the transverse direction on each side of the solute source. The cell dimensions (x, y, z) in the rest of the model domain are of 10 m, 10 m, and 0.5 m respectively (Fig. 1). These cell dimensions, which are applied within numerical solutions, ensure a sufficiently small value of the grid Peclet number (Zheng & Wang, 1999), while at the same time, an acceptable computation demand on CPU.

Sensitivity analysis is performed on the following parameters: effective porosity (n_e), dispersivity (longitudinal $[\alpha L]$, transverse horizontal $[\alpha H]$, transverse vertical $[\alpha V]$), distribution coefficient of sorption processes K_d, where $K_d = f_{oc} \cdot K_{oc}$ (f_{oc} = fractional content of organic carbon, K_{oc} = distribution coefficient of organic carbon-water), and half-life of the substance in the system $(t_{1/2})$. The latter was considered the input parameter for calculation of the chemical decay first-order reaction rate λ $(\lambda = \ln(2)/t_{1/2})$, representing the total decay of the substance by bio-chemical reactions in the environment. The linear, equilibrium method was used to simulate the sorption effect.

The basic settings included the following parameter values: $n_e = 0.2$; $\alpha L = 30$ m, $\alpha H = 3$ m, $\alpha V = 0.3$ m, $K_d = 0.45$ L.kg^{-1} ($f_{oc} = 0.001$; $K_{oc} = 446$ L.kg^{-1}), and $t_{1/2} = 0.3$ r.

The values of physical-chemical properties $(K_{oc}, t_{1/2})$ were set up on the basis of literature data (US EPA, 2012; Zoeteman et al., 1981; Mackay et al., 2006) for ethylbenzene, the monoaromatic hydrocarbon frequently present in contaminated sites.

The basic value of longitudinal dispersivity (αL) was set with regards to the research work of Gelhar et al. (1992). The ratio of $\alpha L/\alpha H/\alpha V$ was maintained with values of 1/0.1/0.01, which is the recommended approach at least for the screening level of investigation (Zheng & Wang, 1999; Bear & Cheng 2010).

The variation of the selected parameter values was kept within "reasonable" ranges, set on the basis of the following literature resources: Morris & Johnson (1967), Bear (1972), Freeze & Cherry (1979), Boonstra & de Ridder (1981), Zoeteman et al. (1981), Gibb et al. (1984), Fetter (1988), Walton (1988), Adams & Gelhar (1992), Kruseman & de Ridder (1994), Aronson & Howard (1997), Suarez & Rifai (1999), Wiedemeier et al. (1996, 1999), Lu & Zheng (2003), Román-Blanco (2003), Mackay et al. (2006), She at al. (2006), Delgado (2007), US EPA (2012), Urumovič & Urumovič (2016).

The following parameters remained unchanged during the entire calculation: hydraulic conductivity $k = 5.0$ x 10^{-3} m.s^{-1}, groundwater head gradient $i = 0.002$. The mentioned values were set for an alluvial environment based on the work of Zatlakovič et al. (2017, 2018, 2019, 2020).

The constant concentration of the solute source (C_0) has a dimensionless value of 1. The resulting concentration (C) throughout the model domain has a dimensionless – relative value of C/C_0 (0 – 1).

Three reference points are defined to record the resulting modelled concentrations (Fig. 2). The first point is situated on the plume centerline, at the transport distance of 200 m from the solute source. The second point is located at a distance of 50 m from the first point in a horizontal direction, perpendicular to the direction of groundwater flow. Finally, the third point is situated at a distance of 5 m, below the first reference point.

3. RESULTS

3.1. Comparison of results for the basic setting of selected parameters and source geometry

The solute concentrations computed numerically with the MOC and TVD advection solver used (hereafter as MOC and TVD method) are the highest at all the selected reference points,
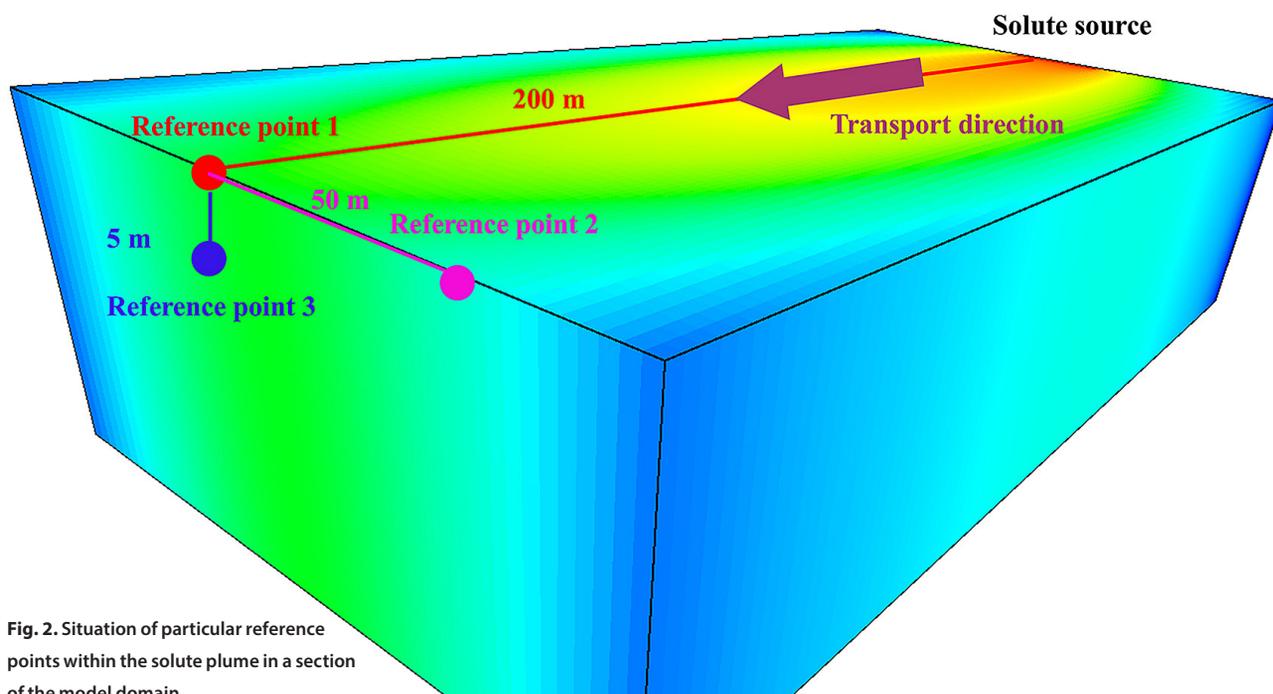
Fig. 2. Situation of particular reference points within the solute plume in a section of the model domain.

differing significantly from the lower concentrations computed by analytical methods and the Step-method. The resulting concentrations of the numerical scheme with an FDI advection solver (hereafter as the FDI method) can be found among the mentioned groups of method with their values (Fig. 3).
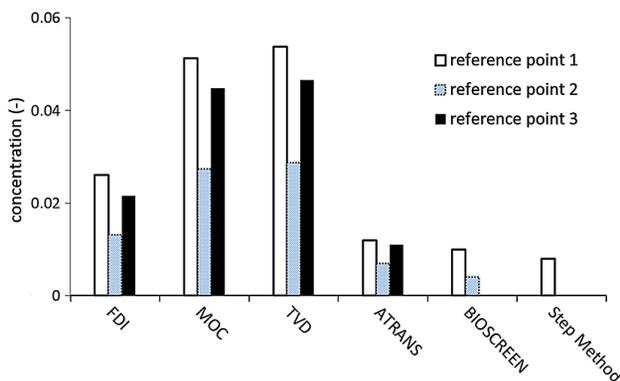
Fig. 3. Solute concentration at individual reference points, calculated by the selected methods for the basic settings of the parameters and source geometry.

3.2. Sensitivity of the individual methods with respect to selected parameters

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Effective Porosity

The initially-defined effective porosity of 0.2 was subsequently replaced by the values of 0.1 and 0.3 respectively, while all other parameters were left in the basic setting of values. The resulting solute concentration at the individual reference points decreased with increasing effective porosities (Fig. 4), revealing a similar picture to basic parameter settings (Fig. 3). The highest solute concentrations were obtained by the numerical TVD and MOC methods, whereas all other methods yielded lower concentrations.

The calculated solute concentrations by non-numerical methods converge with increasing effective porosity (Fig. 4).

The maximum solute concentration difference of 0.014 within one method ($\Delta 1$ in Fig. 4 and similarly in figures 5, 6, 7, 9) was indicated for the ATRANS method at reference point 1 (Tab. 1; Fig. 8). This method is therefore, the most sensitive to the variations of effective porosity among all the examined methods. In turn, the least sensitive is the Step-method, showing a difference of only 0.002 (Tab. 1; Fig. 8). The maximum difference in the calculated solute concentrations between individual methods ($\Delta 2$ in Fig. 4 and similarly in figures 5, 6, 7, 9) was recorded at reference point 1 with the value of 0.051, for an effective porosity value of 0.1 between the Step-method and the TVD method. This value significantly exceeds the value of the difference in the calculated solute concentration by one method (0.014), which means that the choice of calculation approach may fundamentally affect the calculated solute concentration more than the variability of effective porosity value used.

Dispersivity

The basic values of dispersivity (longitudinal-transverse horizontal-transverse vertical) of 30 m – 3 m – 0.3 m were replaced by 7 m – 0.7 m – 0.07 m and 80 m – 8 m – 0.8 m, while all other parameters were left in the basic values. The distribution of the calculated solute concentrations as a function of dispersivity is shown in Fig. 5, which highlights a different trend of variations in the calculated solute concentrations between the numerical and other methods. Whereas the numerical methods follow a directly proportional trend, the analytical methods and the Step-method show an inversely proportional trend within the range of low dispersivity (Fig. 5). The resulting concentrations calculated by the numerical and other methods overlap only in the case of the numerical FDI method for low values of dispersivity (Fig. 5). In turn, no overlap with the results of any non-numerical
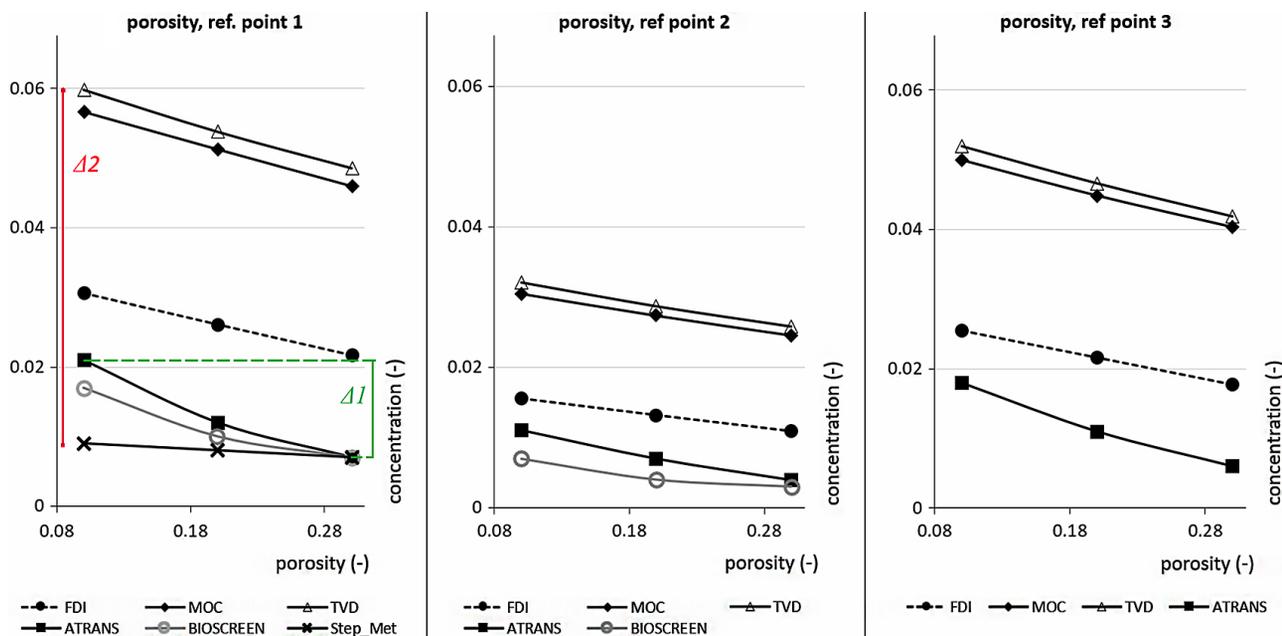
Fig. 4. Solute concentration at individual reference points calculated by selected methods at selected values of effective porosity, with explanatory depiction of the evaluated differences.

method for any value of dispersivity was observed in the case of the MOC and TVD methods. The calculated concentrations by the MOC and TVD methods were always significantly higher than in the case of the other methods.

The maximum solute concentration difference of 0.055 within calculation by one method was indicated for the FDI method at reference point 1 (Tab. 1; Fig. 8), which means that the FDI method is the most sensitive to dispersivity. In contrast, the least sensitive to a given parameter at reference point 1 is the Step-method with the difference value of 0.003. A smaller difference value was recorded at reference point 2 for Domenico's model with the value of 0.002 (Tab.1; Fig. 8). It is important to note here that at reference points 2 and 3, the Step-method cannot be applied.

The maximum difference of 0.07 in the calculated solute concentration between the results of individual methods was recorded at reference point 1, for the dispersivity of 80 m – 8 m – 0.8 m between the TVD method and Domenico's analytical solution. This value exceeds the value of the difference in the solute concentration calculated by one method (0.055), which means that the choice of calculation approach may fundamentally affect the calculated solute concentration more than the used variability of dispersivity.

Performance of Domenico`s solution in comparison with the ATRANS method in this case reveals an inconsistency. At reference point 1 is Domenico`s solution more sensitive, while at reference point 2, the more sensitive is the ATRANS method. This is in agreement with the findings of Guyonnet & Neville (2004), Srinivasan et al. (2007) and West et al. (2007) – with regards to the debatable performance of Domenico's approximate solution in some circumstances.

Distribution coefficient K_d

The basic K_d value of 0.45 L.kg^{-1} was replaced by the values of 0.225 L.kg^{-1} (50 % reduction) and 0.9 L.kg^{-1} (100 % increase)

Tab. 1. The methods sensitivity to parameters expressed by the differences between the calculated solute concentrations at the minimum and maximum parameter level within the defined ranges (source table of Fig. 8).

Reference point 1	porosity	dispersivity	Kd	$t_{1/2}$	SUM
FDI	0.009	0.055	0.0484	0.06	0.172
MOC	0.011	0.03	0.0555	0.069	0.166
TVD	0.011	0.029	0.0563	0.071	0.167
ATRANS	0.014	0.009	0.0109	0.016	0.05
BIOSCREEN	0.01	0.017	0.01	0.013	0.05
Step Method	0.002	0.003	0.0114	0.014	0.03
Reference point 2	porosity	dispersivity	Kd	$t_{1/2}$	SUM
FDI	0.005	0.033	0.0256	0.032	0.096
MOC	0.006	0.026	0.031	0.039	0.102
TVD	0.006	0.049	0.0314	0.040	0.126
ATRANS	0.007	0.003	0.007	0.008	0.025
BIOSCREEN	0.004	0.002	0.005	0.005	0.016
Reference point 3	porosity	dispersivity	Kd	$t_{1/2}$	SUM
FDI	0.008	0.053	0.0421	0.053	0.156
MOC	0.01	0.043	0.05	0.063	0.166
TVD	0.01	0.043	0.051	0.064	0.168
ATRANS	0.012	0.003	0.011	0.014	0.04

Explanations: FDI – finite difference implicit method, MOC – method of characteristics, TVD – total variation diminishing method, Kd – distribution coefficient of sorption, t1/2 – solute half-life in the environment.

respectively, while all other parameters were maintained at the initial level. The distribution of the calculated concentrations as a function of K_d is shown in Fig. 6, indicating the highest values for the numerical methods MOC and TVD, medium
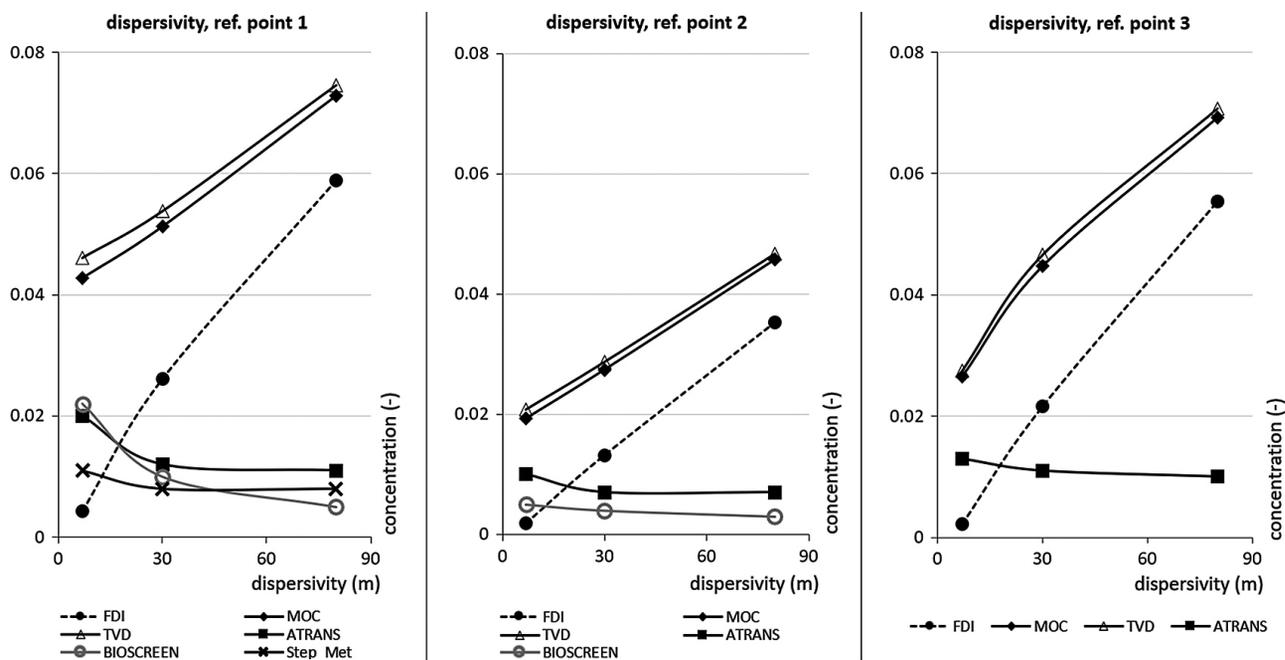
Fig. 5. Solute concentration at individual reference points calculated by selected methods for selected values of dispersivity.
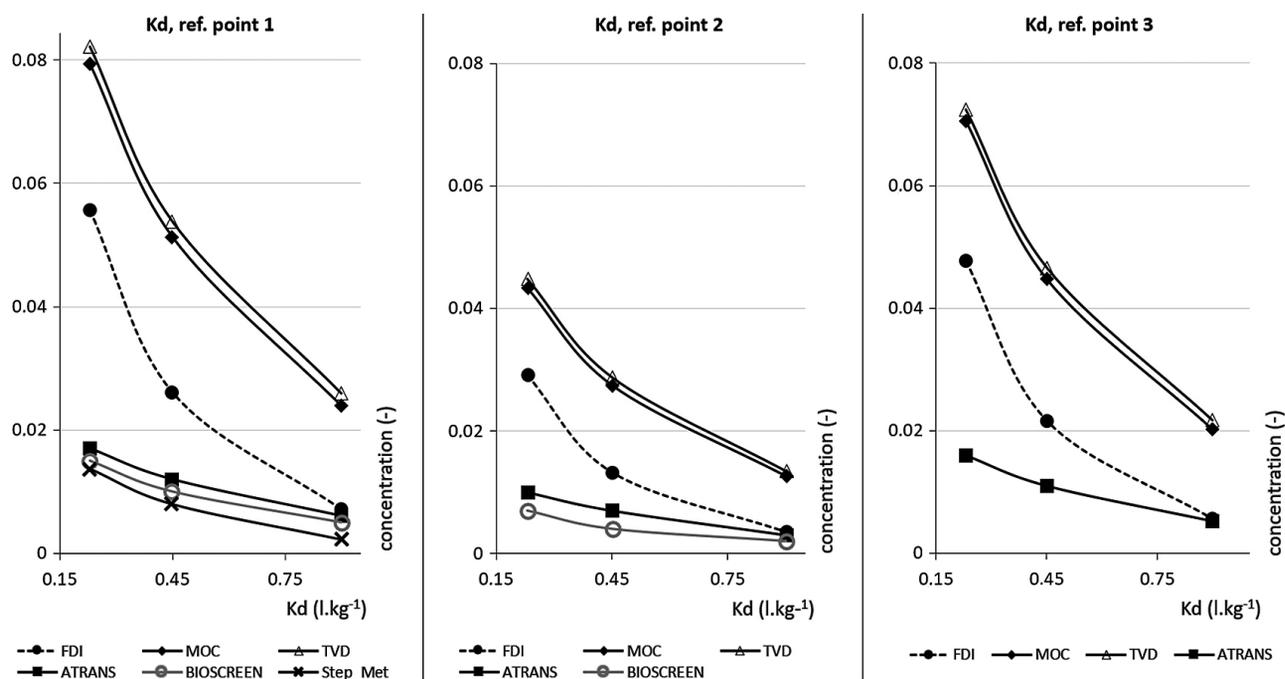
Fig. 6. Solute concentration at individual reference points calculated by the selected methods at selected values of K_d.

values for the numerical FDI method, and the lowest values for the non-numerical methods. The difference between the calculated solute concentration between the numerical and other methods decreases with increasing K_d. The resulting solute concentrations are almost identical at the maximum K_d level in the case of the numerical FDI and non-numerical methods (Fig. 6).

Within a given variation of K_d, the TVD method showed the maximum difference in the solute concentration calculated by one method with the value of 0.056, recorded at reference point 1 (Tab. 1; Fig. 8). This method is therefore the most sensitive to the

parameter K_d, whereas Domenico's analytical solution appears to be the least sensitive with the difference value of 0.005. The maximum difference, 0.069 at reference point 1 in calculated solute concentrations using different methods, resulted from the comparison of the Step-method and the TVD method for the minimum K_d value (0.225 L.kg^{-1}). The difference in the calculated solute concentrations between the numerical and other methods was inversely proportional to the K_d value at all reference points (Fig. 6). The choice of the calculation approach may significantly affect the calculated solute concentration more than the selected variability of the K_d.

Half-life of the substance in the environment

The basic value of the substance half-life $t_{1/2}$ (0.3 y) was replaced by the values 0.15 y and 0.6 y (50 % and 200 % of the initial value) respectively. All other parameters remained unchanged. The distribution of the calculated concentrations as a function of the $t_{1/2}$ value is shown in Fig. 7. The calculated solute concentrations at all the reference points are directly proportional to $t_{1/2}$ in all of the examined methods. The resulting solute concentration calculated by the numerical FDI and analytical ATRANS methods overlap at reference point 2, for $t_{1/2}$ = 0.15 r (Fig. 7).

The maximum difference (0.071) in the solute concentration calculated by one method was indicated for the TVD method at reference point 1 for $t_{1/2}$ = 0.6 y (Tab. 1; Fig. 8). This reveals that the TVD is the most sensitive method with respect to $t_{1/2}$.; The greatest difference in solute concentrations with respect to different methods was observed between the TVD method

and the Step-method with a value of 0.077 at reference point 1, for the $t_{1/2}$ value of 0.6 y. The least sensitive method was Domenico's analytical method with a minimal difference of 0.005 at reference point 2.

The magnitude of the difference in the calculated solute concentration between the numerical and other methods was directly proportional to the value of $t_{1/2}$ at all reference points (Fig. 7). The $t_{1/2}$ parameter was shown to be the most influential among the tested parameters within the set conditions (Tab. 1; Fig. 8).

Overall additive sensitivity of the methods

Overall additive sensitivity of individual methods to selected parameters was evaluated by summation of the differences between the calculated solute concentrations at the minimum and maximum parameter level for every parameter and every method used (Tab.1; Fig. 8). The most sensitive is the numerical
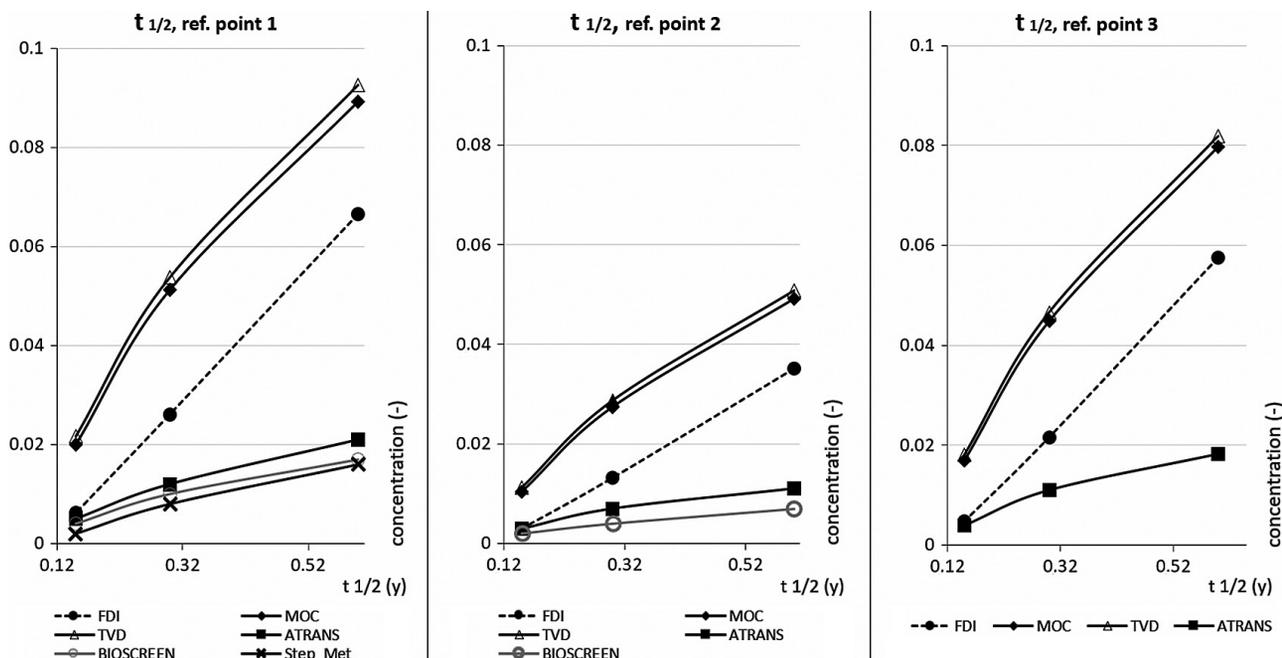
Fig. 7. Solute concentrations at the individual reference points calculated by selected methods at the selected values of $t_{1/2}$.
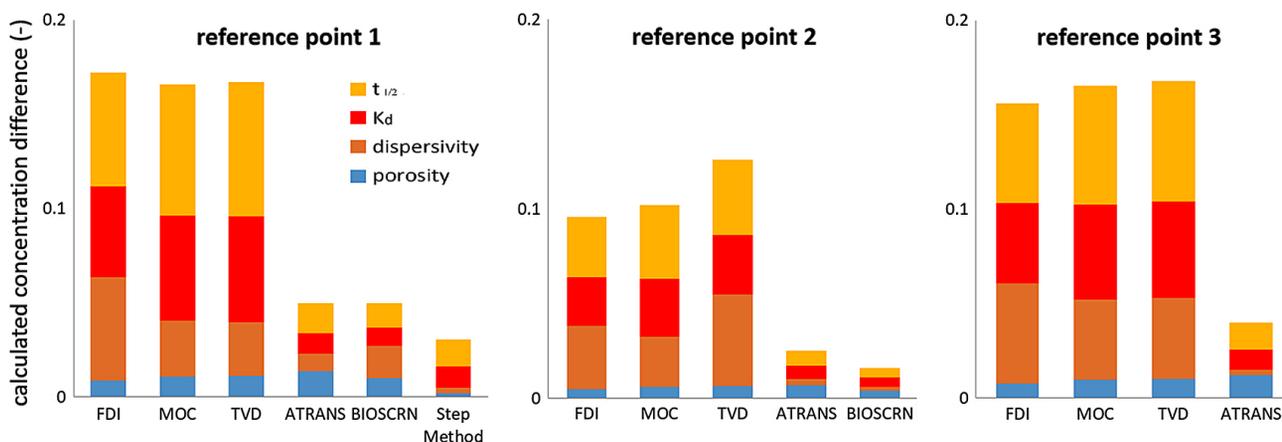
Fig. 8. The methods sensitivity to parameters expressed by the differences between the calculated solute concentrations at the minimum and maximum parameter level within the defined ranges.

scheme with the FDI advection solver at the plume centerline (reference point 1). The least sensitive is Domenico`s solution outside of the plume centerline (reference point 2). In comparison with the ATRANS model, Domenico's solution is significantly less sensitive outside the plume centerline then on it, which correlates with the findings of Guyonnet & Neville (2004) on biased performance of Domenico`s solution outside the plume centerline in some conditions.

3.3. Synergistic effect of the parameters

Transport simulations were also performed with simultaneous change of all examined parameter values (effective porosity, dispersivity, distribution coefficient, half-life of the substance) to determine the minimizing (optimistic approach) and maximizing (conservative approach) synergistic effect on the calculated solute concentrations. The results were also compared with the results obtained for the basic parameter settings (Fig. 9).

The maximal difference in the solute concentration calculated within one method was recorded for the TVD method at reference point 1, with a value of 0.153. The maximum difference in the calculated solute concentration between the individual selected methods was recorded at reference point 1 for the conservative setting between the TVD method and the Step-method, with a value of 0.123.

It can therefore be concluded that the parameter settings with synergistic effect may be more influential than the computational method selection.

The difference in the calculated solute concentration between the numerical and other methods was larger for the conservative strategy than for the optimistic strategy at all reference points. By the synergistic effect, the calculated solute concentration, computed by any method, approaches zero within the optimistic setting (Fig. 9).

The most sensitive method to the synergistic effect of selected parameters is the numerical TVD method at all reference points. The least sensitive method is Domenico`s model at reference point 2.

At reference point 1, Domenico's solution is more sensitive

than the ATRANS model. In contrast, at reference point 2, the ATRANS model is more sensitive than Domenico`s solution (Fig. 9). This inconsistency correlates with the findings of Guyonnet & Neville (2004) on biased performance of Domenico`s solution outside the plume centerline in some conditions.

It can be concluded that numerical schemes are generally more sensitive and conservative than analytical methods, including the Step-method under the conditions analyzed.

The maximal difference in the solute concentration calculated within synergistic effect by one method with a value of 0.153 differs from the overall additive sensitivity, evaluated in the previous chapter, with maximal value of 0.172 for FDI method, what confirms the non-linearity of the problem.

In addition, the synergistic effect leads to the different sensitivity ranking of the used methods than the overall additive sensitivity evaluation in the previous chapter by summation of the concentration differences for particular parameter and method (Tab. 1; Fig. 8).

3.4. Impact of the source thickness

The impact of the solute source thickness (depth of penetration below groundwater surface) on the match between the calculated solute concentrations by the numerical TVD scheme and the analytical ATRANS method was investigated. The evaluated solute source thicknesses were 0.5 m, 2 m, 7 m, and 15 m. The thickness of the aquifer was constantly 15 m. The computed results are demonstrated in Fig. 10 as the resulting dimensionless concentration against ratio of the solute source thickness and the aquifer thickness denoted in %.

The highest correlation of the results at all reference points was achieved with source thickness of about 7 % of the aquifer thickness. With a smaller source thickness, a more conservative solution was identified with the TVD scheme. In contrast, the ATRANS method appears more conservative with a thicker source. The difference between these methods increases with an increase of the solute source thickness above 7 % of the aquifer thickness. The ATRANS method performs with higher sensitivity to the source thickness (Fig. 10).
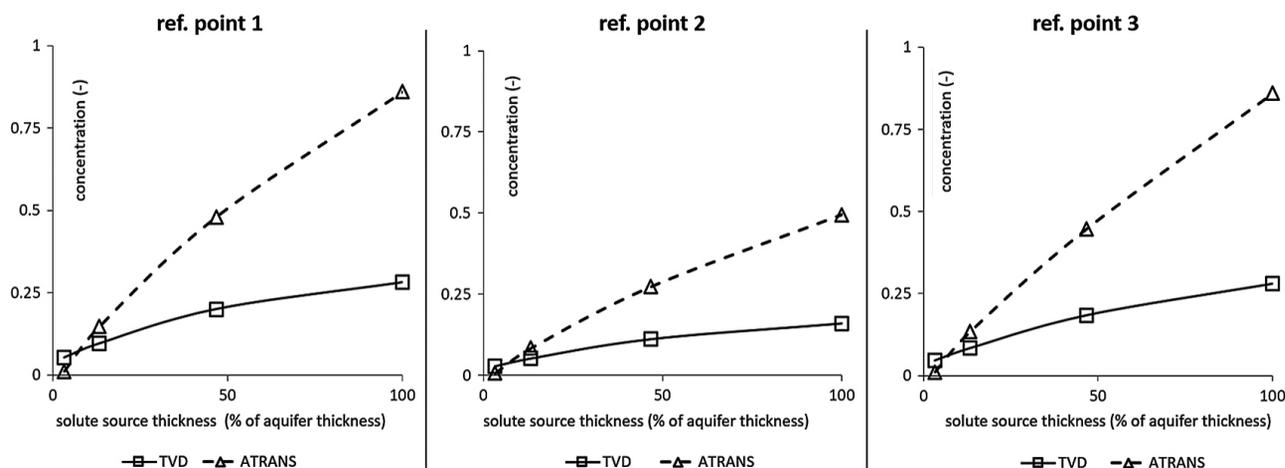
Fig. 9. Solute concentration at individual reference points calculated within the analysis of the synergistic effect of selected parameters with conservative, basic, and optimistic settings of parameter values.
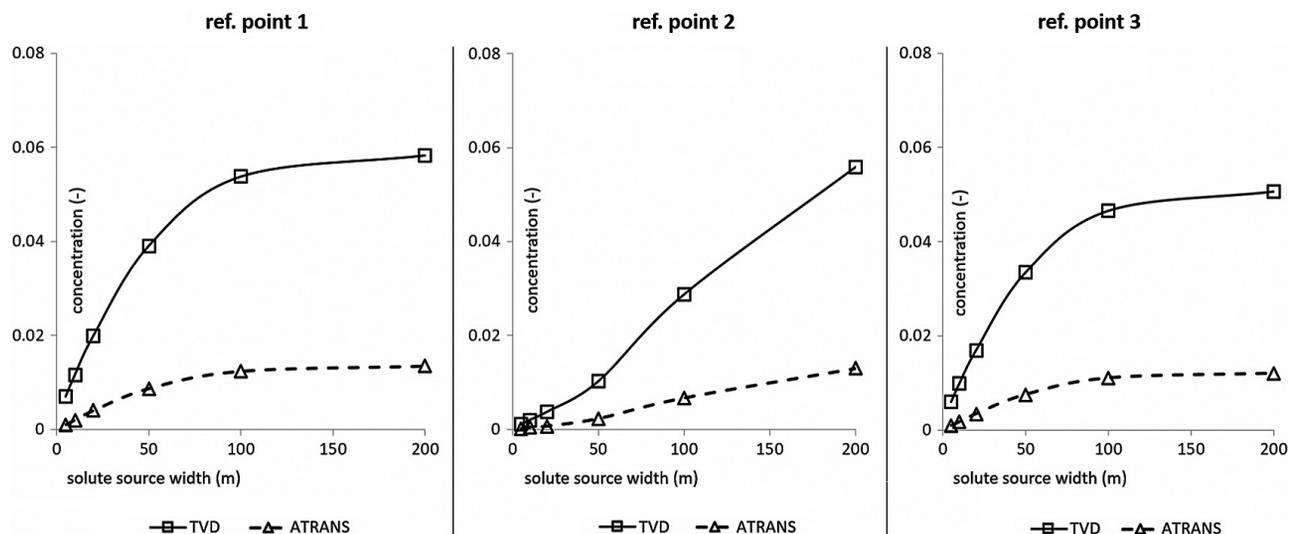
Fig. 10. Dependence of the calculated concentration by the TVD and ATRANS methods on the ratio of the source thickness and the aquifer thickness.

3.5. Impact of the source width

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The width of the solute source was investigated as a possible factor affecting the correlation of the results between the numerical and analytical methods, which were employed to address the effect of source thickness. The sequence of source width 5 m – 10 m – 20 m – 50 m – 100 m – 200 m was applied, while the dimensions of model domain were left unchanged. From the results shown in Fig. 11, it can be concluded that the source width change does not affect the difference between the results obtained by the numerical TVD scheme and the ATRANS analytical method as fundamentally as the source thickness does. The differences rise up to 4.5, 4.3 and 3.9 % of the source concentration at reference points 1, 2, and 3 respectively.

With increasing width of the solute source up to 100 m, the difference between the results increases significantly at all reference points; the calculated solute concentration by the TVD method always being higher than the concentration computed by the ATRANS method. The increase of the solute source width above 100 m causes a lower increase rate of the

difference between the results at reference points 1 and 3. In turn, the difference increase rate at reference point 2 remains approximately constant (Fig. 11). This phenomenon likely depends on the ratio between the source width and the reference point distance from the plume centreline, as well as from the solute source.

4. CONCLUSIONS

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Within the presented comparative study, the transported solute concentrations were calculated by means of selected numerical and analytical methods, as well as the Step-method. The simulations were performed for various values of selected physical-chemical transport parameters and various source dimensions. Obtained results allowed for comparison of the sensitivity between individual methods to selected transport parameters. The easily-accessible and widely-used software, MT3DMS, ATRANS and BIOSCREEN were used.

It can be concluded that the used numerical schemes with
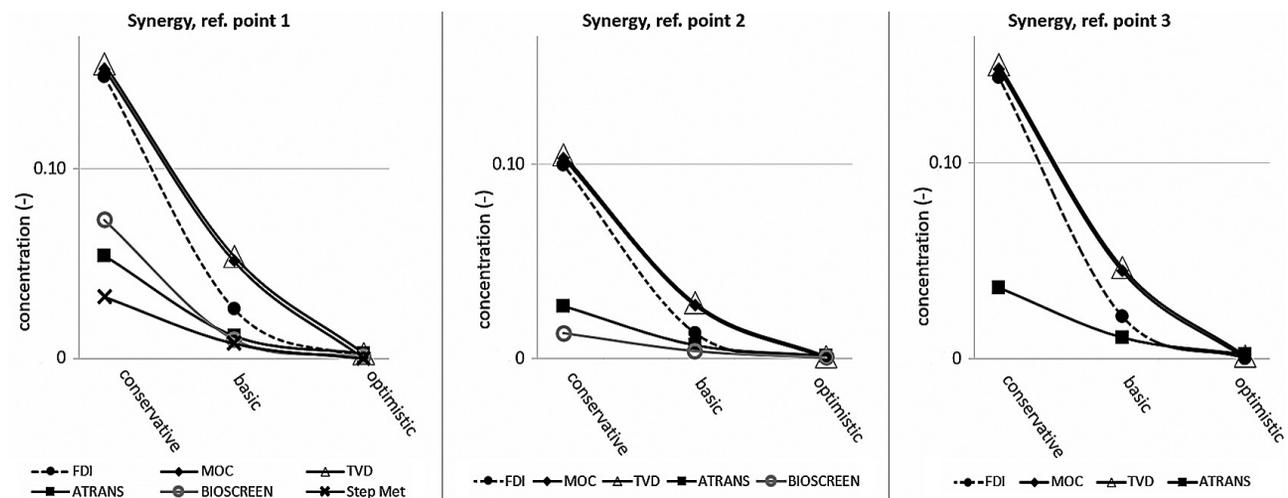
Fig. 11. Dependence of the calculated solute concentrations by the TVD and ATRANS methods on the width of the solute source.

TVD, MOC, and FDI advection solvers (TVD, MOC, and FDI methods) under the defined conditions compute higher concentrations in comparison with the analytical solutions of Domenico (1987) and Newille (2005), including the Step-method. The only exception was recorded in the case of the minimal value of the K_d parameter, where the lowest calculated concentration at all reference points are recorded for the numerical FDI method.

It can also be concluded that the numerical schemes demonstrate an overall higher sensitivity to the inspected transport parameters. The exception is the effective porosity parameter, to which the ATRANS analytical method is the most sensitive.

One important finding is the different trend of changes in the calculated solute concentrations with dispersivity changes. The solute concentration obtained by numerical models is directly proportional to the value of the dispersivity at all reference points. In contrast, an indirect proportion can be observed for analytical methods and the Step-method within low dispersivity values range.

Within presented conditions, the substitution of the numerical MOC and TVD methods, for the analytical or Step-method can produce a higher impact on the resulting concentration than the change of individual parameter values within applied ranges.

The synergistic effect of inspected parameters (simultaneous change of their values to maximize or minimize calculated concentration) shows a more pronounced effect on the calculated solute concentration than the effect of a substitution in calculation method.

The highest correlation between the results of the TVD and ATRANS method at all reference points was achieved for the solute source thickness (depth of penetration) about 1.05 m, which represents about 7 % of the aquifer thickness. Smaller source thickness led to the concentrations calculated by the TVD method to be higher; larger source thickness led to the concentration calculated by ATRANS method to be higher. The maximum difference between the results of these methods is 58 % of the concentration in the solute source, which was reached in the case of fully penetrating the solute source. The analytical ATRANS method was more sensitive with respect to the solute source thickness.

The difference between the TVD and ATRANS results is directly proportional to the width of solute source and reaches value up to 4.5 % of the concentration at the source. The calculated solute concentration by the TVD method is always higher at all reference points.

Despite the fact, that both schemes are 3D transport solutions, the difference between their outcomes can considerably vary depending on the source dimensions. The source thickness (depth of penetration) reveals to be fundamentally important, more than the source width. The hypothesis on the strong correlation between numerical and analytical computational procedures was not confirmed in the case of source geometry impact on the computed results.

The presented results stress the importance of solute transport modelling always by means of several available methods in order to get an idea of the variability of possible results. It is also necessary to determine the transport parameters in-situ. Their database/literature values can vary enough to significantly affect the modeling results, especially in the case of their synergistic effect. In the case of parameter uncertainties, it is reasonable practice to model the worst possible scenario. The spatial characteristics of the solute source must be thoroughly investigated on each site and consider its effect on the computed results with respect to the chosen computation method.

We also conclude that the Step-method cannot provide acceptable results nor be recommended for any stage of investigation study in practice.

References

Adams E. E. & Gelhar L. W., 1992: Field study of dispersion in a heterogeneous aquifer 2. Spatial moments analysis. *Water Resources Research*, 28, 12, 3293–3307.

Antelmi M., Renoldi F. & Alberti L., 2020: Analytical and numerical methods for a preliminary assessment of the remediation time of pump and treat systems. *Water*, 12, 2850, 1–25.

Aronson D. & Howard P. H., 1997: Anaerobic biodegradation of organic chemicals in groundwater: A summary of field and laboratory studies. Final report. Environmental Science Center Syracuse Research Corporation, New York, 263 p.

Batu V., 1996: A generalized three-dimensional analytical solute transport model for multiple rectangular first-type sources. *Journal of Hydrology*, 174, 57–82.

Batu V., 2006: Applied flow and solute transport modeling in aquifers: Fundamental principles and analytical and numerical methods. CRC Press, Boca Raton, Florida, 696 p.

Bear, J., 1972: Dynamics of fluids in porous media. American Elsevier Publishing Company, New York, 756 p.

Bear J. & Cheng A. H. D., 2010: Modeling groundwater flow and contaminant transport. Springer, Netherlands, 834 p.

Bear J. & Verruijt A., 1987: Modeling groundwater flow and pollution. D. Reidel Publishing Company, Netherlands, 414 p.

Boonstra J. & de Ridder N. A., 1981: Numerical modeling of groundwater basins. International Institute for Land Reclamation and Improvement. Netherlands, 226 p.

Delgado J. M. P. Q., 2007: Longitudinal and transverse dispersion in porous media, *Chemical Engineering Research and Design*, 85 (A9), 1245–1252.

Domenico P. A., 1987: An analytical model for multidimensional transport of a decaying contaminant species. *Journal of Hydrology*, 91, 49–58.

Estabragh A. R., Pereshkafti M. R. S. & Javadi A. A., 2013: Comparison between analytical and numerical methods in evaluating the pollution transport in porous media. *Geotech & Geology Engineering*, 31, 93–101.

Fetter C. W., 1988: Applied Hydrogeology. Merril Publishing Company, Ohio, 592 p.

Freeze R. A. & Cherry, J. A., 1979: Groundwater. Prentice-Hall, Inc., New Jersey, 604 p.

Gelhar L. W., Welty C. & Rehfeldt K. R., 1992: A critical review of data on field-scale dispersion in aquifers. *Water Resources Research*, 28, 7, 1955–1974.

Guyonnet D. & Neville C., 2004: Dimensionless analysis of two analytical solutions

for 3-D solute transport in groundwater. *Journal of Contaminant Hydrology*, 75, 141–153.

Gibb J. P., Barcelona M. J., Ritchey J. D. & LeFaivre M. H., 1984: Effective porosity of geologic materials, Annual report, Illinois State Water Survey, 40 p.

Harbaugh A. W., 2005: MODFLOW-2005, The U.S. Geological Survey modular ground-water model – the ground-water flow process: U.S. Geological Survey Techniques and Methods 6- A16, Virginia, variously p.

Huyakorn P. S., Ungs M. J., Mulkley L. A. & Sudicky E. A., 1987: A three-dimensional analytical method for predicting leachate migration. *Groundwater*, 25, 5, 588–598.

Krčmář D., Fľaková R., Ondrejková I., Hodasová K., Rusnáková D., Ženišová Z. & Zatlakovič M., 2020: Assessing the impact of a heated basement on groundwater temperatures in Bratislava, Slovakia. *Groundwater*, 58, 3, 406–412.

Kruseman G. P. & de Ridder N. A., 1994: Analysis and evaluation of pumping test data. International Institute for Land Reclamation and Improvement, Netherlands, 377 p.

Leij F. J., Skaggs T. H. & Van Genuchten M. T., 1991: Analytical solutions for solute transport in three-dimensional semi-infinite porous media. *Water Resources Research*, 27,10, 2719–2733.

Lu G. & Zheng Ch., 2003: Natural attenuation of fuel hydrocarbon contaminants: Correlation of biodegradation with hydraulic conductivity in a field case study. Lawrence Berkeley National Laboratory, Open Access Publications from the University of California, 6 p.

Mackay D., Shiu W. Y., Ma K-CH. & Lee S. CH., 2006: Physical-chemical properties and environmental fate for organic chemicals. Taylor & Francis Group, LLC, Florida, 443 p.

Méndez J. H., 2008: Implementation and verification of the USGS solute transport code MT3DMS for roundwater heat transport modelling. Thesis, University of Tübingen, 73 p.

Ministry of the Environment of the Slovak Republic, 2015: Guideline no. 1/2015 –7 On risk analysis of contaminated site elaboration., 96 p.

Molenkamp CH. R., 1968: Accuracy of finite-difference methods applied to the advection equation. *Journal of Applied Meteorology and Climatology*, 7, 160–167.

Morris D. & Johnson A., 1967: Summary of hydrologic and physical properties of rock and soil materials, as analyzed by the hydrologic laboratory of U. S. Geological Survey 1948–1960, U. S. Geological Survey, Washington D. C., 42 p.

Newell C., Mcleond R. & Gonzales J., 1996: BIOSCREEN, Natural attenuation decision support system, User's Manual Version 1.3., U. S. EPA, Washington D. C., 65 p.

Newille C. J., 2005: ATRANS: Analytical solutions for three-dimensional solute transport from a patch source, Version 2, S. S. Papadopulos & Associates, Inc., Ontario, 48 p.

Ogata A., 1970: Theory of dispersion in a granular medium. U.S. Geological Survey, Professional Paper 411-I, Washington D.C., 34 p.

Ogata A. & Banks, R. B., 1961: A solution of the differential equation of longitudinal

dispersion in porous media. U. S. Geological Survey, Professional Paper 411-A, Washington D. C., 7 p.

Pophillat W., Attard G., Bayer P., Méndez J. H. & Blum P., 2018: Analytical solutions for predicting thermal plumes of groundwater heat pump systems, *Renewable Energy*, in press, 1–12.

Román-Blanco L. de S., 2003: Dynamics of gravel and mixed, sand and gravel beaches. Thesis, University of London, 310 p.

Singh M. K., Singh V. P. & Das P., 2016: Mathematical modeling for solute transport in aquifer. *Journal of Hydroinformatics*, 18, 3, 481–499.

She K., Horn D. & Canning P., 2006: Porosity and hydraulic conductivity of mixed sand-gravel sediment. Conference Paper, 16 p.

Srinivasan V., Clement T. P. & Lee K. K., 2007: Domenico solution - is it valid? *Groundwater*, 45, 2, 136–146.

Suarez M. P. & Rifai H. S., 1999: Biodegradation rates for fuel hydrocarbons and chlorinated solvents in groundwater, *Bioremediation Journal*, 3:4, 337–362.

Szucs P., Szekely F. & Zakanyi B., 2013: Comparison of analytical and numerical approaches for simulating groundwater flow to multi screen wells. *Carpathian Journal of Earth and Environmental Sciences*, 8, 2, 69–76.

Urumovič K. & Urumovič K. Sr., 2016: The referential grain size and effective porosity in the Kozeny–Carman model. *Hydrology and Earth System Sciences*, 20, 1669–1680.

U. S. EPA., 2012: Estimation Programs Interface Suite™ for Microsoft Windows, v 4.11. United States Environmental Protection Agency, Washington D.C.

Van Genuchten M. T. H., 1977: On the accuracy and efficiency of several numerical schemes for solving the convective-dispersive equation. Pentech Press, London, 1.71–1.90.

West M. R., Kueper B. H. & Ungs M. J., 2007: On the use and error of approximation in the Domenico (1987) solution. *Groundwater*, 45, 2, 126–135.

Walton W. C., 1988: Practical aspects of groundwater modeling. National Water Well

Association, Ohio, 587 p.

Wexler E. J., 1992: Analytical solutions for one-, two-, and three-dimensional solute transport in ground-water systems with uniform flow. Techniques of. water-resources investigations of the United States Geological Survey, Chapter B7, Washington D.C., 190 p.

Wiedemeier T. H., Swanson A. M., Wilson J. T., Kampbell D. H, Miller R. N. & Hansen J., 1996: Approximation of biodegradation rate constants for monoaromatic hydrocarbons (BTEX) in ground water, U. S. EPA papers, Digital Commons @ University of Nebraska, Nebraska, 26 p.

Wiedemeier T. H., Wilson J. T., Kampbell D. H, Miller R. N. & Hansen, J. E., 1999: Technical protocol for implementing intrinsic remediation with long-term monitoring for natural attenuation of fuel contamination dissolved in groundwater. Air Force Center for Environmental Excellence, Texas, variously paged.

Zatlakovič M., Augustovič B., Bugár A., Durdiaková Ľ., Gavuliaková B., Greš P., Guman D., Krebs P., Kuric P., Marenčák Š. & Mozoli T., 2020: Bratislava – Slovnaft XIII - Geological survey and remediation works for groundwater hydraulic protection in upper Žitný ostrov. Interim report, VÚRUP, a. s., Unpublished Report, archive of ŠGÚDŠ Bratislava, 156 p. [in Slovak]

Zatlakovič M., Durdiaková Ľ., Gavuliaková B., Greš P., Guman D., Kuric P., Marenčák Š., Mozoli T. & Tomasch M., 2019: Bratislava – Slovnaft XIII - Geological survey and remediation works for groundvater hydraulic protection in upper Žitný ostrov. Interim report, VÚRUP, a. s., Unpublished Report, archive of ŠGÚDŠ Bratislava, 154 p. [in Slovak]

Zatlakovič M., Durdiaková Ľ., Gavuliaková B., Kuric P., Marenčák Š., Mozoli T., Pažitný B. & Tomasch M., 2018: Bratislava – Slovnaft XIII - geological survey and remediation for groundwater hydraulic protection system in upper part of Žitný ostrov. Interim report, VÚRUP, a. s., Unpublished Report, archive of ŠGÚDŠ Bratislava, 120 p. [in Slovak]

Zatlakovič M., Durdiaková Ľ., Kadeřábek J., Marenčák Š., Mozoli T., Pažitný B., Pikalíková L. & Tomasch M., 2017: Bratislava – Slovnaft XIII - geological survey and remediation for groundwater hydraulic protection system

in upper part of Žitný ostrov. Interim report, VÚRUP, a. s., Unpublished Report, archive of ŠGÚDŠ Bratislava, 151 p. [in Slovak]

Zheng C. & Wang P. P., 1999: MT3DMS: A modular three-dimensional multi-species transport model for simulation of advection, dispersion, and chemical reactions of contaminants in ground-water systems; documentation and user's guide, Contract Report SERDP-99-1, U. S. Army Engineer Research and Development Center, Mississippi, 207 p.

Zoeteman B. C. J., Greef E. D. & Brinkmann F. J. J., 1981: Persistency of organic contaminants in groundwater, lessons from soil pollution incidents in the Netherlands. *Science of The Total Environment*, 21, 187–202.