Experimental Verification of the Contaminant Transport in the Aquifer Incorporating Advection, Dispersion and Sorption Processes

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Abstract

The paper addresses the site verification of the practical 2D-mathematical model of conservative and passive contaminant transport in the groundwater stream incorporating also, except the advection and dispersion processes, the source (negative) term of reversible sorption. It is generally assumed, that local equilibrium conditions exist between the aqueous (free)-phase and the solid (sorption)-phase for the sorption process being considered. For such an equilibrium-controlled state, the term of reversible sorption can be described by the linear or non-linear adsorption (desorption) isotherms in relation to statics of this process. In this analysis the Freundlich equilibrium isotherm was accepted, which is also widely applied in practice. In this 2D-mathematical model the numerical solution (using the finite difference method), calculated values of the longitudinal and transverse dispersion coefficients (D_x, D_y) as well as the adsorption parameters (K, N) were used. To facilitate the numerical solutions, the modified calculation programme "PCCS-1" was also worked out. The calculated maximal values of chloride concentrations based on this model were compared with the measured chloride concentrations in those selected for this verification piezometers installed in the natural aquifer. The calculated values of relative deviations (between the calculated and the measured concentrations in relation to the measured concentrations) proved the sufficient accuracy of the numerical solution of the contaminant transport model in groundwater stream presented with the non-linear source term representing the adsorption process. The calculations proved also the low adsorption capacity in the aquifer selected for verification. The site verification of the presented 2D-mathematical model of contaminant transport in ground medium proved the possibility of practical usage of this model for engineering calculations of the contaminant concentration fields in the natural aquifers.

Key words: advection, diffusion (dispersion), reversible sorption (adsorption – desorption), contaminant transport, numerical solution, site verification.

1. Introduction

The paper addresses the site verification of the presented 2D-mathematical model of conservative and passive contaminant transport in the aquifer compared with the presented numerical solution of the site surveys results of the contaminant substance concentrations. With the exception of the advection and dispersion processes, 2D-model of contaminant transport in groundwater stream presented incorporates the source (negative) term of reversible sorption.

It is generally assumed, that local equilibrium conditions exist between the aqueous (free)-phase and the solid (sorption)-phase for the sorption process being considered. For such an equilibrium-controlled state, the term of reversible sorption can be described by the linear or non-linear adsorption (desorption) isotherms in relation to the statics of this process.

In the model presented the Freundlich equilibrium adsorption isotherm was accepted as the source (negative) term of the reversible sorption. This type of the adsorption isotherm is also widely applied in practice (Szperliński 1981, Kowal 1990, Chiang and Kinzelbach 2001, Logan 2001).

Practical use of the presented 2D-mathematical contaminant transport model depends on identification of the required ground, hydraulic, dispersion and the Freundlich non-linear isotherm parameters in this equation (Kleczkowski et al. 1984, Kowal 1990, Chiang and Kinzelbach 2001, Logan 2001).

2. Description and Solution of the Contaminant Transport Equation in Groundwater Stream

To describe the conservative and passive contaminant transport incorporating the reversible sorption term, the well-known 2D-advection-diffusion equation was used, resulting from the transport continuity equation (Szperliński 1981):

$$\frac{\partial C}{\partial t} + u_x = D_x \frac{\partial^2 C}{\partial x^2} = D_y \frac{\partial^2 C}{\partial y^2} - \frac{\rho}{m} \frac{\partial S}{\partial t}, \tag{1}$$

where:

C – the solute concentration in flowing groundwater in aqueous phase (in the local equilibrium conditions),

S – the mass of the solute species adsorbed on the grounds per bulk dry mass unit of the porous medium (in local equilibrium conditions),

u_x – the component of the average (real) seepage velocity in pore space along the x axis (as pore velocity),

D_x – the component of the longitudinal dispersion coefficient along the x axis,

D_y – the component of the transverse dispersion coefficient along the y axis,

ρ –   the bulk density of the porous medium,

m –   the effective porosity of the porous medium,

t –   the co-ordinate of time,

x, y –   the co-ordinates of the assumed reference system.

In equation (1), assuming one-dimensional flow of groundwater along the x axis, both the components of the average (real) seepage velocities in pore space ($u_y = u_z = 0$) and the advection terms ($u_y \partial C/\partial y = u_z \partial C/\partial z = 0$) were neglected in the other y and z axes.

In this analysis the final 2D-transport equation (1) was accepted in relation to the slotted contaminant outflow ($\partial C/\partial z = 0$), because as it resulted from observations by the users of these ground lagoons filled with liquid manure, the formed cracks of the geotextile had, for the modelling case, a vertical slot shape on the whole thickness of the aquifer (*Results . . .* 1982). So, the dispersion term along the vertical z axis ($D_z \partial^2 C/\partial z^2$) can be treated as negligible ($D_z \partial^2 C/\partial z^2 = 0$), simulating in the further analysis the longitudinal ($D_x \partial^2 C/\partial x^2$) and the transverse ($D_y \partial^2 C/\partial y^2$) dispersion of flowing contaminant mass in the aquifer.

The longitudinal and transverse dispersion coefficients (D_x and D_y) which are being considered in the equation (1), called also hydrodynamic dispersion coefficients, assume the form:

$$\left. \begin{array}{l} D_x = \alpha_L \cdot u_x + \tau \cdot D_M \\ D_y = \alpha_T \cdot u_x + \tau \cdot D_M \end{array} \right\}, \tag{2}$$

where:

α_L, α_T –   the constants of the longitudinal and transverse dispersivity along the x and y axes,

D_M –   the molecular (effective) diffusion coefficient,

τ –   the dimensionless tortuosity parameter of the porous medium.

Basing on the equation (2) the hydrodynamic dispersion coefficients (D_x and D_y) are given by the terms representing mechanical dispersion coefficients $\alpha_L \cdot u_x$ and $\alpha_T \cdot u_x$ and effective (modified) molecular diffusion $\tau \cdot D_M$ (Fried 1975, Kleczkowski et al. 1984, Chiang and Kinzelbach 2001, Logan 2001).

The constants of the dispersivity α_L and α_T depend on the scale (length) of contaminant region spreading in the aquifer. In the regional scale, for the length of spreading $L > 100$ m, the constant α_L should be identified with the size of the ground medium heterogeneity also as macrodispersion process (Kleczkowski et al. 1984, Chiang and Kinzelbach 2001). Basing on the literature site surveys it results, that value of this constant will increase together with increasing of the way (length) of contaminant migration region (as the scale effect, Fried 1975,

Anderson 1979, Kleczkowski et al. 1984, Gelhar et al. 1992, Spitz and Moreno 1996).

Simultaneously, based on these site surveys results, the values of the constant of the transverse dispersivity α_T should be accepted in the scope of $\alpha_T = (0.05 \div 0.2) \, \alpha_L$ (Kleczkowski et al. 1984, Kleczkowski and Różkowski 1997, Chiang and Kinzelbach 2001, Logan 2001).

Whereas, the temperature-dependent values of the molecular (effective) coefficients D_M are generally very low in the scope of $D_M \cong 1 \cdot 10^{-9} \div 2 \cdot 10^{-9} \, \text{m}^2 \cdot \text{s}^{-1}$, basing both on the numerous laboratory research and the site surveys for the various graining (porosity) of the ground media being considered. Thus, in most cases it can be neglected in calculations of the hydrodynamic dispersion coefficients acc. to Eq. (2), (Li and Gregory 1974, Chiang and Kinzelbach 2001).

The tortuosity parameter τ, which generally expresses the solute mass flow along longer available pathways through the pore space is dependent both on the graining and effective porosity of the porous medium. The numerical values of the tortuosity parameter τ are in the wide scope of $0.7 \div 0.01$ adequate to the structure of the ground media being considered (Robinson and Stokes 1965, Kleczkowski et al. 1984, Freeze and Cherry 1979, Chiang and Kinzelbach 2001, Logan 2001).

Simultaneously, basing on both the experimental research and the site surveys for laminar movement of groundwater, the turbulent diffusion process can also be neglected (Macioszczyk and Szestakow 1984, Chiang and Kinzelbach 2001, Logan 2001).

The last term in the equation (1) $- \partial S / \partial t$ represents generally the negative source term of the reversible sorption (as the adsorption-desorption system) connected with the mass exchange phenomenon, which expresses general relationship $\partial S / \partial t = f(C, S)$ between the mass of the solute species adsorbed on the grounds per bulk dry mass unit of the porous medium S and the solute concentration in flowing groundwater in the aqueous phase C (Travis 1978, Szperliński 1981, Bear and Veruijt 1987, Chiang and Kinzelbach 2001).

Basing on the numerous experimental and site surveys on the reversible sorption process, this process can be found to be one of the factors giving the highest reduction of the conservative contaminants spreading in ground medium (Travis 1978, Szperliński 1981, Macioszczyk and Szestakow 1984, Bear and Veruijt 1987, Kowal 1990, Chiang and Kinzelbach 2001, Logan 2001).

However, the reduction scale of these contaminants as the result of the reversible sorption (as the adsorption-desorption system) depends, among the other things, on both physico-chemical properties of the spreading contaminants (as adsorbate) and the ground media (as adsorbent), as well as on the scale of the laboratory or site research carried out (Travis 1978, Macioszczyk and Szestakow 1984, Kleczkowski et al. 1984, Kowal 1990).

Assuming the local equilibrium condition between phases – aqueous (free) and sorption (solid) – function $S = f(C)$ implicates, that the sorption term $\partial S/\partial t$ in equation (1) can be replaced by the expression $\partial S/\partial C \cdot \partial C/\partial t$.

Thus, taking into account the above remark and by factoring out the term $\partial C/\partial t$, the equation (1) may be written in the form:

$$\frac{\partial C}{\partial t}\left(1 + \frac{\rho}{m} \cdot \frac{\partial S}{\partial C}\right) + u_x\frac{\partial C}{\partial x} = D_x\frac{\partial^2 C}{\partial x^2} + D_y\frac{\partial^2 C}{\partial y^2}. \tag{3}$$

As the result of literature review in the case of reversible sorption assumption (as a negative source term) in the advection-diffusion equation (3) by the $\partial C/\partial t$ term, the constant dimensionless expression will always be found, which in literature is known as the retardation factor R in the form (Travis 1978, Barovic 1979, Szperliński 1981, Bear and Veruijt 1987, Chiang and Kinzelbach 2001, Logan 2001):

$$R = 1 + \frac{\rho}{m} \cdot \frac{\partial S}{\partial C}. \tag{4}$$

As results from the equation (3), the retardation factor R makes a certain modification (reduction) of the average (real) seepage velocity in pore space u_x/R compared with the value of this velocity in the case of neglection of this factor (u_x).

Linearity or non-linearity of the retardation factor R in the equation (3), and at the same time the form of the modified average seepage velocity in pore space u_x/R will result from the assumed descriptions of the reversible physical sorption process, through use of the empirical equations of the adsorption (desorption) isotherms in relation to statics of this process.

In the paper, the well-known empirical equation of the Freundlich isotherm was accepted, for assumption of the local equilibrium of concentrations. For such equilibrium-controlled state, it can be assumed that the rate of the reversible adsorption process is equal to zero ($\partial S/\partial t = 0$) in relation to the ground medium with the finite sorption capacity (for the constant temperature and negligible value of the irreversible chemical sorption), (Chiang and Kinzelbach 2001, Logan 2001).

In the case of analyzing the mono-layered adsorption process on the assumption that the number of the adsorbed particles for the complete covering of the ground grain surface (as adsorbent) cannot be greater than the number of the so-called "active places", the mathematical notation of the adsorption process is considered according to the Freundlich non-linear isotherm by the following equation (Travis 1978, Barovic 1979, Bear and Veruijt 1987, Kowal 1990, Chiang and Kinzelbach 2001, Logan 2001):

$$S = K \cdot C^N, \tag{5}$$

where:

K, N – the parameters of the Freundlich isotherm ($K-$ as the Freundlich constant, N – as the Freundlich exponent, that depends on the solute species, nature of the porous medium and other conditions of the system).

In addition to the the Freundlich non-linear isotherm (5) accepted in this analysis, the retardation factor R acc. to Eq. (4) assumes adequately the form:

$$R = 1 + \frac{\rho}{m} \cdot \frac{\partial S}{\partial C} = 1 + \frac{\rho}{m} \cdot N \cdot K \cdot C^{N-1}. \tag{6}$$

However, assuming the lack of the local equilibrium state, it may be accepted, that sorption process rate does not equal zero ($\partial S / \partial t \neq 0$) in relation, for example, to the porous medium with very great sorption capacity. In such state for the mathematical description of sorption models the kinetic models should be used (as the reversible I-order or N-order models of kinetics), defining at the same time the velocity constants of the adsorption (k_1) and the desorption (k_2) processes (Szperliński 1981, Kowal 1990, Chiang and Kinzelbach 2001, Logan 2001).

In relation to the reversible I-order model of kinetics, the equation takes the form:

$$\frac{\partial S}{\partial t} = \frac{m}{\rho} \cdot k_1 \cdot C - k_2 \cdot S = k_2 \cdot \left[\frac{m}{\rho} \cdot \frac{k_1}{k_2} \cdot C - S \right], \tag{7}$$

instead, in the case of the reversible N-order model of kinetics, adequate equation takes the form:

$$\frac{\partial S}{\partial t} = k_2 \left[\frac{m}{\rho} \cdot \frac{k_1}{k_2} \cdot C^N - S \right], \tag{8}$$

where:

k_1 – the velocity constant of adsorption process,
k_2 – the velocity constant of desorption process.

Taking into account both equation (6) and the expression $1 + \rho/m = A_0$, the advection-diffusion equation (3) may be written in the form:

$$\frac{\partial C}{\partial t} + \frac{u_x}{A_0 \cdot N \cdot K \cdot C^{N-1}} \frac{\partial C}{\partial x} = \frac{D_x}{A_0 \cdot N \cdot K \cdot C^{N-1}} \frac{\partial^2 C}{\partial x^2} +$$

$$+ \frac{D_y}{A_0 \cdot N \cdot K \cdot C^{N-1}} \frac{\partial^2 C}{\partial y^2}. \tag{9}$$

Equation (9) can be given by the dimensionless form:

$$\frac{\partial C^*}{\partial \tau} + \frac{1}{A_0 \cdot A \cdot (C^*)^{N-1}} \frac{\partial C^*}{\partial \xi} =$$

$$= \frac{D_x^*}{A_0 \cdot A \cdot (C^*)^{N-1}} \frac{\partial^2 C^*}{\partial \xi^2} + \frac{D_y^*}{A_0 \cdot A \cdot (C^*)^{N-1}} \frac{\partial^2 C^*}{\partial \eta^2}, \tag{10}$$

taking into account the dimensionless parameters:

$$\left.\begin{array}{l} \dfrac{x}{L} = \xi; \ \dfrac{y}{L} = \eta; \ \dfrac{C}{C_0} = C^*; \ \dfrac{u_x t}{L} = \tau; \\[2mm] \dfrac{D_x}{u_x L} = D_x^* \ \dfrac{D_y}{u_x L} = D_y^*; \ N \cdot K \cdot C_0^{N-1} = A \end{array}\right\}, \tag{11}$$

where:

- L – the distance from the source of the contaminant outflow (injection) to the last calculated ground-cross section in the ground medium, treated as the known length of the solution area in the numerical calculations of the transport equation,
- C_0 – the initial contaminant concentration in the source of the outflow (injection) to the ground medium, treated as the known initial concentration in the numerical calculations of the transport equation.

For numerical solution of the presented equation (10), the initial and boundary dimensionless conditions were assumed in the form:

– initial condition:

$$C^*_{(0 \leq \xi \leq \infty, \ 0 \leq \eta \leq \infty, \ \tau=0)} = 0, \tag{12}$$

– boundary conditions:

$$\left.\begin{array}{l} C^*_{(\xi=0, \ \eta=0, \ \tau>0)} = 1 \\[2mm] C^*_{(\xi=0, \ \eta\neq0, \ \tau>0)} = 0 \\[2mm] C^*_{(\xi\to\infty, \ -\infty \leq \eta \leq \infty, \ \tau>0)} = 0 \end{array}\right\}. \tag{13}$$

In the numerical calculations of the dimensionless concentration values in case of occurrence of the background concentration C_n in the groundwater stream, both the initial condition (12) and the boundary conditions (13) should be applied just as for the zero-value of the background concentration ($C_n = 0$).

However, in the case of occurrence of the background concentrations $C_n \neq 0$ the dimensionless values of the calculated contaminant concentrations C^* acc. to

Eq. (10) take the form $C^* = (C - C_n)/(C_0 - C_n)$, otherwise by neglecting the background concentrations, the adequate form $C^* = C/C_0$.

First derivatives in the equation (10) were approximated by the reverse difference quotients and second derivatives by the symmetrical difference quotient, (Szymkiewicz 2000).

Thus, equation (10) may be written as:

$$\frac{C^*_{i,j,r} - C^*_{i,j,r-1}}{w^*} + \frac{1}{1 + A \cdot (C^*)^{N-1}} \cdot \frac{C^*_{i,j,r} - C^*_{i-1,j,r}}{h^*} =$$

$$= \frac{D^*_x}{1 + A \cdot (C^*)^{N-1}} \cdot \frac{C^*_{i+1,,j,r} - 2C^*_{i,j,r} + C^*_{i-1,j,r}}{(h^*)^2} + \tag{14}$$

$$+ \frac{D^*_y}{1 + A \cdot (C^*)^{N-1}} \cdot \frac{C^*_{i,j+1,r} - 2C^*_{i,j,r} + C^*_{i,j-1,r}}{(k^*)^2},$$

where:

h^*, k^*, w^* – the dimensionless grid steps of the presented differential scheme according to ξ, η and τ directions.

In further equations the asterisk symbol for the concentration values was neglected ($C^* = C$), assuming also, that the examined calculation node grid, according to equation (10), is situated in the saturated zone between the free hydraulic gradient and the aquifer floor (Aniszewski 2001).

In the case of the numerical solution of equation (10) with the non-linear adsorption term, it is possible to obtain the final non-linear system of the equations in the form (Szymkiewicz 2000):

$$Y(C) \cdot C = B, \tag{15}$$

where:

$Y(C)$ – the matrix of the rates depending on changeable values of the concentrations C,

C – the vector created from the node concentration values,

B – the vector of absolute terms.

The linearization consisting in calculation of the matrix rates $Y(C)$, based on the concentrations from the previous time step was made for solution of the system of the equations (15):

$$Y(C)_t \cdot C_{t+\Delta t} = B, \tag{16}$$

The solution algorithms of the non-linear equations according to the equation (10) were realised in the form of the modified computational programme "PCCS – 1", giving the dimensionless values of the contaminant concentrations in the range $< 0, 1 >$.

The general algorithm of the modified "PCCS – 1" computational programme was presented by Aniszewski (2001).

3. Characteristics of the Aquifer and the Indicator Chosen for the Site Verification being Considered

From among many conservative indicators being considered in the site surveys made by the Institute of Environmental Development in Poznań (chlorides, sulfates, phosphates) for the presented site verification of the equation (10), describing contamination transport in the aquifer, the chlorides were selected generally, in spite of the relatively low adsorbing capacity of this indicator in relation to granular materials (Woods 1978).

Despite of lower chloride adsorbing capacity (for example in relation to the sulfates or pesticides), the literature contains many papers, which authors determining the physical adsorption influence also used chlorides as the conservative (refractive) contamination (Barovic 1979, Macioszczyk and Szestakow 1984, Hassanizadeh et al. 1990, Kleczkowski et al. 1984).

Basing on the general literature analysis, it can be concluded, that the chloride adsorbing capacities will be relatively greater both in the case of their flow in natural aquifers with relatively small graining (for example in sandy ground media) and in the case of occurrence in these natural aquifers admixtures of the various substances, for example with microporous structure, increasing the adsorbing capacities of the aquifers (Kowal and Świderska-Bróż 1997).

According to the literature research received up to now, the chloride concentration change as the conservative indicator is mainly caused by the physical adsorption process (except in the case of simultaneous advection and dispersion processes).

It should also be noted, that the chemical and biological processes are less important in relation to the chlorides and can generally be neglected in the mathematical transport models (Barovic 1979, Van Genuchten et al. 1974, Chiang and Kinzelbach 2001).

Acceptance of the chlorides in this presented site verification also proves the fact, that in the natural groundwater stream also occur calcium bicarbonates, which can react in adequate conditions with inflowing sulfate ions, creating insoluble (precipitating) calcium sulfates in quantities not easily expected.

It was also assumed, that both the quantity of possible substance being created as the result of the biodegradation process and its adsorbing capacity in relation

to the chlorides, are so low in comparison with the mass of the natural deposit, selected for verification and its adsorption capacity, that they can be neglected.

The chlorine in the natural organic compounds occurs only in vestigial quantities as opposed, for example, to the sulphur compounds.

Thus, for the presented site verification, it was assumed that processes which can be considered to be the result of liquid manure biodegradation, do not affect the values of the analysed chloride concentrations to any considerable degree.

The site observations in the natural ground medium adjoining the existing breeding farm "Redło" nearby Świdwin in the West Pomeranian Voivodeship, were used for verification (*Results . . . 1982*).

The source of groundwater contamination in this ground medium constituted the seven ground lagoons filled with the prepurified on the vibrating screens liquid manure.

The visual observations of these lagoons conducted by their user confirmed the feasibility of vertical cracking of the geotextile and direct leaking of the liquid manure into the groundwater stream (especially from ground lagoon number 4 – Fig. 1, *Results . . . 1982*).

For the exact examination of the contamination transport in this groundwater stream, a certain number of piezometers was installed near the existing ground lagoons with their concentration in particular, near ground lagoon number 4.

All piezometers selected for the site verification were installed by the Geotechnical Office "Geoprojekt" (*Technical . . . 1981*).

Basing on these existing piezometers, the Institute of Environmental Development in Poznań tested the concentration values of the selected contamination indicators in the natural groundwater stream, collecting the water samples in these piezometers (*Results . . . 1982*). The three selected measurement series were finally carried out in 1981–1982.

During this testing, the concentration values of the selected contamination indicators were also measured in the samples collected directly in the ground lagoons, filled with liquid manure (treated at the same time as the initial concentration C_0, *Techno-Economic . . . 1986*).

At the same time, in the presented site verification, the zero-value of chloride background concentrations ($C_n = 0$) in groundwater stream were also assumed, basing on the accessible site measurements, according to (*Results . . . 1982*).

The Institute of Environmental Development in Poznań made each time the measurements of the background concentrations C_n in the groundwater stream for the selected indicators just before the every planned measure series, also taking into account the chlorides concentrations, which were practically close to zero.

In the case of lack of such research, the certain disturbance caused by the occurrence of these background concentrations ($C_n \neq 0$) should be taken into account in the transport model (Eq. 10) by use the presented earlier initial (Eq. 12)

and boundary (Eq. 13) conditions and by accepting the dimensionless concentration values C^* in the presented form $C^* = (C - C_n)/(C_0 - C_n)$.

These background concentrations C_n could also influence the contamination transport process in the natural ground medium in relation to their site measurements.

The detailed location of the four piezometers selected for the site verification, together with their numeration and the distances between them, is presented in Fig. 1 (Aniszewski 2001, *Technical* ... 1981).
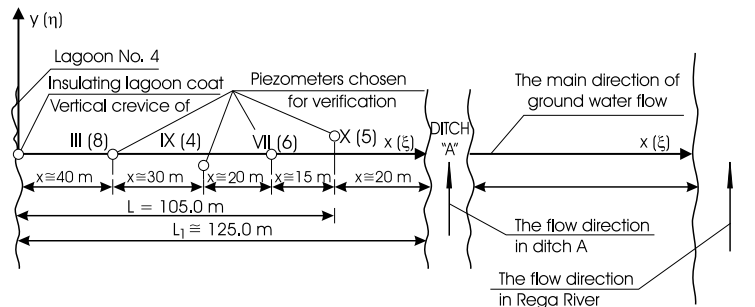
Fig. 1. Location of the piezometers selected for the site verification of the equation (10)

4. Identification of the Parameters in the Transport Equation

Practical usage of the presented dimension (Eq. 3) or the dimensionless (Eq. 10) contaminant transport equations in the groundwater stream depends on identification of the required parameters in these equations, which can be divided into the adequate groups (Kleczkowski et al. 1984, Chiang and Kinzelbach 2001), given below.

4.1. The Ground and Hydraulic Parameters of the Porous Medium

The parameters characterizing the ground and hydraulic properties of the ground medium (the average seepage velocity in pore space as pore velocity u_x, the effective porosity of the porous medium m, the bulk density of the porous medium ρ), should be defined basing on own or the literature site surveys carried out in the natural aquifers.

Taking into account the above remark, the values of these parameters were accepted basing on the measurements made by "Geoprojekt" in the natural ground medium, selected for the site verification (*Technical* ... 1981). So, it can be noted, that these parameters are verified basing on the field experiment for preserving both the real conditions of the groundwater flow and the real porosity, as well as the density of the ground medium on a natural scale. The numerical values of these parameters are $u_x \cong 1.13 \cdot 10^{-3}$ m·s^{-1}, $\rho \cong 1.74$ g · m^{-3} and $m \cong 0.37$ (37.0 %), respectively acc. to (*Technical* ... 1981).

In the case of determination of the parameters u_x, m and ρ, basing on the laboratory research, the consideration of the geometric scale-dependent similarity for the selected region of the contaminant transport would be necessary (Gelhar et al. 1992).

4.2. The Contaminant Dispersion Parameters in the Groundwater Stream

The contaminant dispersion coefficients (D_x and D_y) should be calculated acc. to Eq. (2), using the earlier determined parameters u_x, α_L and α_T basing on own or the literature site surveys, carried out in the natural aquifers and simultaneously, for the negligible low values of the molecular diffusion coefficient D_M and at the same time for the negligible low values of the effective molecular diffusion term $\tau \cdot D_M$ in the equation (2).

Basing on the analyzed literature, the numerical value of the constant of the longitudinal dispersivity α_L required in equation (2) is $\alpha_L \cong 7.0$ m for the real length of the spreading region $L \cong 105.0$ m in relation to the sandy ground media having the similar values of the effective grain size d_{10} and effective porosity m to the ground selected for site verification (Kleczkowski et al. 1984, Kleczkowski and Różkowski 1997, Gelhar et al. 1992, Spitz and Moreno 1996, Chiang and Kinzelbach 2001).

Based on the practical scope of the values of the constants of the transverse dispersivity α_T accepted in literature, the numerical value of this constant required in equation (2) is $\alpha_T \cong 0.05 \cdot \alpha_L \cong 0.05 \cdot 7.0$ m $\cong 0.35$ m, respectively (Fried 1975, Anderson 1979, Kleczkowski et al. 1984, Gelhar et al. 1992, Spitz and Moreno 1996, Chiang and Kinzelbach 2001).

Thus, accepting the values of the parameters u_x, α_L and α_T determined earlier, the numerical values of the contaminant dispersion coefficients D_x and D_y calculated acc. to Eq. (2) are $D_x \cong 7.93 \cdot 10^{-3}$ m²·s⁻¹ and $D_y \cong 3.96 \cdot 10^{-4}$ m²·s⁻¹, respectively.

In the case of using the values of the contaminant hydrodynamic dispersion coefficients D_x and D_y, calculated basing on the parameters u_x, α_L and α_T in relation to the laboratory research (similarly to the determination of the ground and hydraulic parameters of the ground medium in the laboratory conditions) the consideration of the geometric scale-dependent similarity would be necessary (Gelhar et al. 1992)

4.3. The Parameters of the Freundlich Non-Linear Isotherm

The values of the non-linear adsorption isotherm parameters acc. to Eq. (5) (K, N) in relation to statics of this process, should be calculated basing on the separate static "batch" laboratory experiments (with immobile groundwater) and simultaneously using in these research both similar ground media and the contaminant indicators which will be used in site verifications.

Taking into account the adsorption description considered in this paper in relation to statics of this process in own laboratory research, the "batch" method was used, assuming also the local concentration equilibrium $\partial S/\partial t = 0$. Based on this method the maximal adsorption capacities of the particular ground samples having graining and porosity (d_{10}, m) were determined.

Taking into account the field experiment, accepted in this paper, characterized by the conservative chloride migration acc. to (*Results ...* 1982), in a separate laboratory experiment sodium chloride was also used as the conservative indicator. Thus, in both the laboratory and selected field experiment, the adsorption process concerned the real migration of the chloride anions (Cl^-) in the natural aquifer.

The parameters of the Freundlich non-linear isotherm, obtained in own laboratory tests, are $K \cong 0.4132$ m^3 g^{-1} and $N \cong 0.6122$, respectively.

The possibility of acceptance of the values of the sorption parameters (as the velocity constants of adsorption k_1 or desorption k_2 process) obtained due to dynamic research in the conditions of mobile groundwater, on the columns or ground models, is connected with the earlier description of this process in relation to sorption kinetics, using the description of this process rate by the presented equations of the reversible sorption kinetics as the equations of the *I*-order acc. to Eq. (7) or *N*-order acc. to Eq. (8), adequately (Kleczkowski et al. 1984, Macioszczyk and Szestakow 1984, Chiang and Kinzelbach 2001).

It is fully admissible to use the numerical values of these all parameters ($u_x, m, \rho, D_x, D_y, K$ and N) presented in the subchapters 4.1, 4.2 and 4.3 for the site verification of the transport equations (3) or (10) in relation to the selected natural ground medium without the necessity of determining the geometric scale-dependent similarity (Kleczkowski et al. 1974, Gelhar et al. 1992, Kleczkowski, Różkowski 1997, Chiang, Kinzelbach 2001).

5. The Calculation Results of the Chloride Concentrations

Basing on the previously determined numerical values of the parameters of the contaminant transport equation in groundwater ($u_x, D_x, D_y, m, \rho, K, N$), the numerical calculations of the maximal chloride concentration values were made basing on both the dimensional form of the transport equation (10) and the modified calculation programme "PCCS – 1" (Aniszewski 2001).

In addition, the numerical values of the parameters acc. to Eq. (11) needed for numerical calculations are: $L \cong 105.0$ m (as the measured distance from the edge of ground lagoon number 4 to the last piezometer X (5) (Fig. 1) acc. to *Technical ...* 1981) and $C_0 \cong 296.0$ g $\cdot$ m^{-3}, respectively (as the measured value of the initial chloride concentration in lagoon number 4 acc. to *Techno-Economic ...* 1986).

The rounded calculated values of the contaminant advection times t_c in relation to the particular piezometers ($t_c = x/u_x$) are presented in Table 1.

Table 1. The maximal calculated (Eq. 10) and measured (*Results* ... 1982) dimensionless values of the chloride concentrations in piezometers together with the relative deviation values
(measurement series: November 1981)

Calculated advection time τ_c [dimensionless]		$\tau_c \cong 0.38$ $(t_c \cong 35400$ s$)$ (ca. 9.8 h)	$\tau_c \cong 0.67$ $(t_c \cong 61900$ s$)$ (ca. 17.2 h)	$\tau_c \cong 0.86$ $(t_c \cong 79500$ s$)$ (ca. 22.1 h)	$\tau_c \cong 1.00$ $(t_c \cong 92800$ s$)$ (ca. 25.8 h)
Measurement place (number of piezometer) (acc. to Fig. 1)		III (8)	IX (4)	VII (6)	X (5)
Distance ξ from the source of leakage (as lagoon No. 4) [dimensionless]		0.38 $x \cong 40.0$ m	0.66 $x \cong 70.0$ m	0.86 $x \cong 90.0$ m	1.00 $x \cong 105.0$ m
Initial concentration C_0 (in lagoon No. 4) [dimensionless]		1.00	1.00	1.00	1.00
Values of contamination concentrations [dimensionless]	$C_{\max c}$ Eq. (10)	0.4035 0.4394*	0.2383 0.2536*	0.1758 0.1837*	0.0910 0.0939*
	C_m (*Results* ... 1982)	0.3716	0.2248	0.1502	0.0743
Absolute difference of contamination concentrations $\Delta = \|C_{\max c} - C_m\|$ [dimensionless]		0.0319	0.0135	0.0256	0.0167
Value of relative deviation $\Delta / C_m \cdot 100\%$ [%]		8.6 8.9**	6.0 6.4**	17.1 4.5**	22.5 3.2**

  * – values of the maximal dimensionless concentrations acc. to Eq. (10) – adsorption term (retardation factor R) neglected,

** – the relative deviation between the values of maximal concentrations acc. to Eq. (10) for adsorption term neglected and taken into account.

The maximal values of the chloride concentrations were calculated in the distances resulting from the location of the particular piezometers in the selected ground (Fig. 1, *Technical* ... 1981).

In the numerical solution, the values of dimensionless steps of the difference scheme grid $(\Delta x, \Delta y)$ were determined in relation to the real range scale L of contamination transport (Fig. 1, Aniszewski 2001).

Determining the time step Δt, the value of the Courant number $C_a = 1$ $(C_a = u_x \cdot \Delta t / \Delta x)$ was also assumed in the numerical solution, to eliminate the so-called "numerical" diffusion effect v_n $[v_n = u_x \cdot \Delta x / 2 \cdot (1 - C_a)]$, for both the earlier calculated values of Δx step and the measured average seepage velocity in pore space as pore velocity u_x in the natural aquifer (Aniszewski 2001, Szymkiewicz 2000). The accepted dimensional step values of difference scheme grid Δx, Δy, Δt also satisfied the consistency, stability and convergence conditions of both the presented numerical solution of the equation (10) and the accepted "explicit" calculation scheme (Aniszewski 2001, Szymkiewicz 2000).

The maximal dimensionless values of chloride concentrations calculated numerically acc. to Eq. (10), in distances related to the selected piezometers, were next compared with the measured chloride values in these piezometers for the measure series: November 1981 (*Results ... 1982*). The compilation of the calculated and measured dimensionless values of the chloride concentrations together with the values of the relative deviations are presented in Table 1.

In addition to confirm occurrence of the chloride adsorption capacity in the selected aquifer, the numerical calculations of the chloride concentrations were carried out according to the transport equation (10), simultaneously neglecting in this equation the last adsorption term (Table 1 – values with the asterisk).

Next, the calculated concentration values without the adsorption term (as the greater values) and with the adsorption term (as the lower values) were compared defining the percentage scope of the relative deviations between these concentrations in relation to the lower concentration values with the adsorption term (Table 1 – values with the double asterisk).

The graph of the maximal dimensionless values of both the calculated and measured chloride concentrations in selected piezometers for the measurements from November 1981 is presented in Fig. 2.

Accuracy of the obtained concentration values depends, on the one hand, on the errors connected with the presented transport model and determination of the required parameters in this model.

On the other hand, the certain errors connected with the site surveys method, made by the Institute of Environmental Development in Poznań in the real traverse station (in the natural scale) also occur (*Results ... 1982*).

The measured chloride concentration values obtained in the site research "in situ" acc. to (*Results ... 1982*), took into account the whole complexity of contamination transport in the natural aquifer.

However, the calculated values of relative deviations in the scope of 8.6% ÷ 22.5% between the maximal calculated values according to equation (10) and the measured values according to (*Results ... 1982*) in relation to the measured concentrations, prove the sufficient accuracy of the presented numerical solution of the contamination transport equation (10) in groundwater stream, incorporating also the non-linear negative source term of the adsorption process (Table 1 – values without the asterisk).

The relative deviations in the scope of 3.2% ÷ 8.9% between the values of maximal concentrations acc. to Eq. (10), for adsorption term neglected and taken into account, confirm the fact of occurence of the relatively low, but existing chloride adsorbing capacity in the selected natural aquifer.

The increase of this chloride adsorbing capacities was certainly due to the fact of this conservative indicator flow together with admixtures of other substances in the natural ground having relatively low graining (as sandy ground medium), (Kowal and Świderska-Bróż 1997).
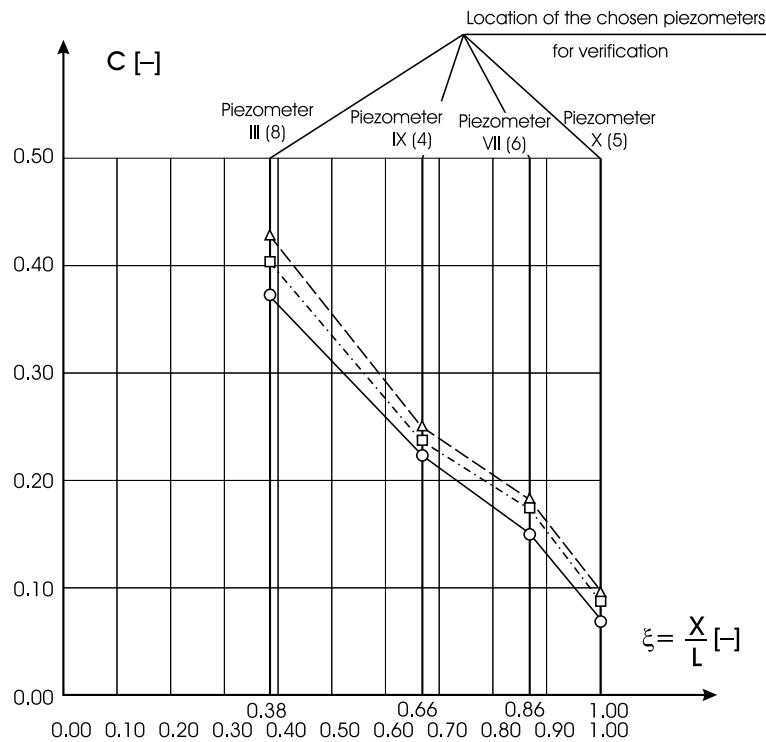
Fig. 2. The values of dimensionless contamination concentrations in the selected piezometers: Δ – the maximal values of the calculated concentrations according to Eq. (10) for negligible adsorption term, □ – the maximal values of the calculated concentrations according to Eq. (10) with incorporated adsorption term, ◯ – experimental values of the measured concentrations according to (*Results ... 1982*)

However, the further site verifications of the presented numerical solution of the transport equation (10) together with defining the transport equation parameters u_x, D_x, D_y, m, ρ, K, N seems to be necessary.

These site verifications should concern both the other kinds of the ground and the other kinds of conservative contaminants having the sorption capacities in the ground medium except chlorides (for example sulfates, phosphates or non-degradable organic compounds such as pesticides).

It will be connected with the greater values of the adsorption term in the contaminant transport equations (greater values of the non-linear adsorption parameters K and N) and with the greater influence of the retardation factor R in these equations, affecting the modified, as the result of the reversible sorption process, average seepage velocity in pore space as pore velocity u_x/R.

It will thereby be affecting a greater reduction of the calculated concentrations, as the result of the sorption process and their approximation to the real measured concentration values in the natural aquifers.

6. Final Conclusions

The presented site verification of the contaminant transport equation in the groundwater stream (10), incorporating simultaneously the non-linear description of the adsorption process, proves the feasibility of its practical application for the engineering calculations of the conservative contaminant concentrations in the natural aquifers.

As proved in the calculations presented, basing on both the transport model and the steady contaminant outflow into the ground medium, in the further cross-sections counting from the source of the outflow, relatively low concentration values C will be received in these cross-sections in relation to the initial concentration values C_0 in the source of contaminant outflow into the ground medium.

Thus, in these further cross-sections low values of the concentration reduction rate which is described in the equation (10) will occur as the last reversible sorption term.

Thus, it can be concluded that the concentration fields in these further cross-sections will behave according to the equation in which occur only the advection and transverse dispersion processes (about the advection genesis). Relatively far from the source of contaminant outflow the term describing sorption process will be negligibly low.

Consideration in the presented mathematical model besides the advection and dispersion processes also the physical non-linear contaminant adsorption process in the flowing groundwater makes the important progress in relation to the existing contaminant transport models in literature hitherto.

It has also a significant practical meaning, for example, in the cases of calculations of the range of the protective zone borders for industrial factories, waste material storage, sewage and sanitary deposit reservoirs (from industrial and agricultural production), as well as for the range of the designing of indirect protective zones for the groundwater intakes.

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