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DESCRIPTION AND VERIFICATION OF THE CONTAMINAT TRANSPORT MODELS IN GROUNDWATER (THEORY AND PRACTICE)

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Abstract: This paper presents a general overview of 2D mathematical models for both the inorganic and the organic contaminants moving in an aquifer, taking into consideration the most important processes that occur in the ground. These processes affect, to a different extent, the concentration reduction values for the contaminants moving in a groundwater. In this analysis, the following processes have been taken into consideration: reversible physical non-linear adsorption, chemical and biological reactions (as biodegradation/biological denitrification) and radioactive decay (for moving radionuclides). Based on these 2D contaminant transport models it has been possible to calculate numerically the dimensionless concentration values with and without all the chosen processes in relation to both the chosen natural site (piezometers) and the chosen contaminants.In this paper, it has also been possible to compare all the numerically calculated concentration values to the measured concentration ones (in the chosen earlier piezometers) in relation to both the new unpublished measurement series of May 1982 and the new set of parameters used in these 2D contaminant transport models (as practical verification of these models).

INTRODUCTION

One can say that many more-or-less complex mechanisms (processes) appear during the flow of contaminants in a groundwater. These processes appearing and overlapping in the ground during contaminant movement should also be mathematically described as the partial more-or-less complex differential models (equations). Afterwards such models (equations) should be used in practice as practical transport models in order to simulate contaminant concentrations in a groundwater. Although the phenomenon of contaminant transport in groundwater flow system is quite well-known and described in the literature (but not to the end) the main problem is related each time to the proper selection of the optimum numerical values of all the parameters used in these equations. All these parameters representing the interactive processes in the ground strongly depend on climatic (temperature) and ground conditions. It is especially related to the parameters representing biological and chemical (radioactive decay) reactions – processes (on aqueous − solid surface) being considered in transport equations. All these reactions (processes) are usually represented as the last terms of these equations (see also the last term $\sum R_n$ in the presented general equation 1).

In various climatic and ground conditions all the numerical parameters used in both the author's and the literature models are quite different. This regularity is related even to the similar (but never the same) contaminants moving in ground media (Spitz and Moreno [9], Chiang [3], Javadi and AL-Najjar [4], Weiss and Cozzarelli [12], Kraft *et al*. [7], Aniszewski [1], Taniguchi and Holman [11], Aniszewski [2]). This is connected, among other things, with negative or positive charging of the solid phase of natural soils (as an "anionic" or "cationic" exchange) (Spitz and Moreno [9], Chiang [3], Javadi and AL-Najjar [4], Weiss and Cozzarelli [12], Kraft *et al*. [7], Taniguchi and Holman [11]). It should also be noted that in various climatic and ground conditions, physico-chemical and biological properties of moving groundwater differ considerably one from another, impacting on all the major processes (parameters) used in the transport models and presented here. The climatic and ground conditions selected for the presented transport models are described in greater detail by Spitz and Moreno [9], Chiang [3], Weiss and Cozzarelli [12], Kraft *et al*. [7], Aniszewski [1], Taniguchi and Holman [11] and Aniszewski [2].

The first important topic of this paper is a presentation of the numerically calculated and the measured concentration values with all the chosen in this paper processes. For the presentation of the numerically calculated concentration values (given in Table 1 and in Fig. 2) both the reduced to 2D domain final transport equations and their numerical solutions were used. The presented here final transport equations take or do not take into consideration all the chosen processes proceeding in natural groundwater. The second topic of this paper is also an exemplary presentation of the measured concentration values as the results taken from the later and as yet unpublished measurement series of May 1982 (given in Table 1 and in Fig. 2). It should be noticed that such late measurement series of May 1982 was taken intentionally to compare among other things the gradual depletion in time of the adsorption capacity of the same ground being considered in this paper (for both this measurement series of May 1982 and for the earlier one of November 1981 – Aniszewski [1], Aniszewski [2]). Based on the numerically calculated and the measured concentration values, in further analysis the following values were calculated:

- ➢ the differences between the numerically calculated concentration values with and without all the chosen processes (as Δ values in Table 2),
- ➢ the differences between the numerically calculated concentration values with and without all the chosen processes and the measured concentration values (also as Δ values in Table 2).

All these calculated differences were the base for final calculations carried out in this paper (as the final purpose):

- ➢ the dimensionless values of concentration reductions as the ratios of the numerically calculated concentration differences to the numerically calculated concentrations (as $\Delta/C^*_{\max c}$ in Table 2),
- ➢ the dimensionless values of concentration reductions as the ratios of differences between thenumerically calculated and the measured concentrations to the measured ones (as $\Delta/C^*_{\max m}$ in Table 2).

All these above-mentioned calculated ratios ($\Delta/C^*_{\max c}$, $\Delta/C^*_{\max m}$) are treated in this paper as standard errors (see in Table 2).

Based on the calculated standards errors given in Table 2 and in general conclusions later in the text one can assess the importance (hierarchy) of the particular processes affecting the concentration reduction during contaminant movement in ground media in relation to the chosen climatic and ground conditions.

The calculated numerically $C^*_{\max c}$ concentrations (where $C^*_{\max c} = C^*_{\max c}/C_o$) are treated in the further analysis as maximal dimensionless ones along the main x (ξ) axis for the y (η) and z axes = 0 (see given below Fig. 1). The explanations of the dimensional $C_{\max c}$ and C_o concentrations are given below in the further part of this paper.

MATERIALS AND METHODS

General Description of the Contaminant Transport and Fate Mechanisms

In the first turn the partial differential governing equation in 3D domain describing the contaminant transport and fate mechanisms of species k_o is presented here. This equation (as mass balance one with the terms of advection, dispersion, adsorption, physico-chemical and biological reactions) is as follows (Spitz and Moreno [9], Zheng and Wang [14], Chiang [3], Zhang *et al.* [13]):

$$\frac{\partial(mC^{k_0})}{\partial t} = \frac{\partial}{\partial x_i}(mD_{ij}\frac{\partial C^{k_0}}{\partial x_j}) - \frac{\partial}{\partial x_i}(mu_iC^{k_0}) + q_sC_s{}^{k_0} + \sum R_n \tag{1}$$

where:

C^{k_0}	the solute concentration in flowing groundwater in aqueous phase (in the localequilibrium conditions) of species k_o [$g\cdot m^{-3}$],
u_i	the component of the so called pore groundwater velocity in pore space [$m\cdot s^{-1}$],
m	the effective porosity of the porous medium [–],
x_i	the distance along the Cartesian co-ordinate axis [m],
D_{ij}	the hydrodynamic dispersion coefficient symmetrical tensor [$m^2\cdot s^{-1}$],
q_s	the volumetric flow rate per unit volume of aquifer representing fluid sources (positive) and sinks (negative) [s^{-1}],
$C_s{}^{k_0}$	the concentration of the source or sink flux for species k_o [$g\cdot m^{-3}$],
t	the co-ordinate of time [s],
$\sum R_n$	the function describing generally biological and chemical reactions treated as queous-solid surface ones [$g\cdot m^{-3}\cdot s^{-1}$] (see that $\sum R_n$ function later in the further parts of this paper).

All the further adopted assumptions along with the adopted set of parameters being considered in equation (1) are presented below in the text. In this analysis one-dimensional flow of groundwater along the x (ξ) axis (with respect to natural groundwater slope along this axis, see also Fig. 1) was assumed. Hence, both the components of the pore groundwater velocities ($u_y = u_z = 0$) and the advection terms ($u_y\partial C/\partial y = u_z\partial C/\partial z = 0$) can also be neglected. In the further analysis both the frequently used in practice real slotted influx of contaminants into the chosen aquifers along the vertical z axis and the concentration equalization along this direction ($\partial C / \partial z = 0$) were also adopted. Hence the dispersion term along this vertical z axis can be set equal to zero ($D_z \partial^2 C / \partial z^2 = 0$). In this analysis, assuming an isotropic ground medium being considered in the chosen real aquifer (in the y and z axes), the simplified form of the hydrodynamic dispersion coefficient symmetrical tensor D_{ij} was accepted. Such assumption is often used in the literature for practical engineering applications (Spitz and Moreno [9], Zheng and Wang [14], Chiang [3], Zhang *et al*. [13]). So, taking into consideration both the above-mentioned assumption and one-dimensional flow of groundwater along the $x\,(\xi)$ axis, the D_{ij} tensor has simplified form, as the longitudinal and transverse dispersion coefficients D_x and D_y (under assumption $D_y \cong D_z$).

The above-mentioned assumptions were related to the site research made by the Institute of Environmental Development in Poznań as the capital of the Greater Poland Province. The source of groundwater contamination in the chosen site (aquifer) was the real ground lagoon (marked by its user as the lagoon 4). This lagoon 4 was filled with the liquid manure from the pig breeding farm "Redło" near Świdwin in the West Pomeranian Province of Poland. The choice of this breeding farm located in the West Pomeranian Province was made intentionally, taking into consideration:

- ➢ the temperate (cold) Polish climatic conditions being considered in this Province,
- ➢ the optimal and characteristic of this region ground and climatic parameters being considered and used in the presented here final transport equations.

For the exact examination of contamination transport into groundwater a certain number of piezometers were installed nearby the existing ground lagoon 4 (Aniszewski [1], Aniszewski [2]). Referring to (Aniszewski [2]), an illustrative map only of the chosen natural site is presented below in Fig. 1 along with the detailed numeration of the existed and chosen four piezometers. These four piezometers were used in the analyzed numerical calculations of the presented here transport models (equations) along with their practical verification. The exemplary dimensionless standard error values $\Delta / C^*_{\max m}$ in relation to the measured concentrations for chlorides and sulfates and referred to the footnote 4 in parentheses are given in Table 2. However, the distances from the ground lagoon 4, as the liquid manure leakage source, to the particular chosen piezometers are presented in Tables 1 and 2 as well as in Fig. 2).

The visual observations of this lagoon 4 conducted by its user confirmed the vertical slotted cracking of geotextile and direct leaking of the liquid manure into groundwater and afterwards movement of this liquid manure in the direction of the Rega river along the main axis $x\,(\xi)$ (see Fig. 1). Basing on the installed piezometers, the Institute of Environmental Development in Poznań measured concentration values of the chosen contamination indicators in the natural groundwater stream (as the C_{m} concentrations), collecting the water samples in these piezometers located near the existing ground lagoon 4. In the further analysis the numerical calculations were related only to the above-mentioned four piezometers located along the main axis $x\,(\xi)$ for axis $y\,(\eta) = 0$ (see Fig. 1).

For these calculations the maximal measured concentration values in the chosen four piezometerswere takeninto consideration (as the $C_{\max m}$ concentrations). Whereas, the calculated numerically dimensional and maximal ($\eta = 0$) concentrations in the chosen four piezometers are treated in the further analysis as the $C_{\max c}$ ones. During these testings, the concentration values of the chosen contamination indicators were also measured in

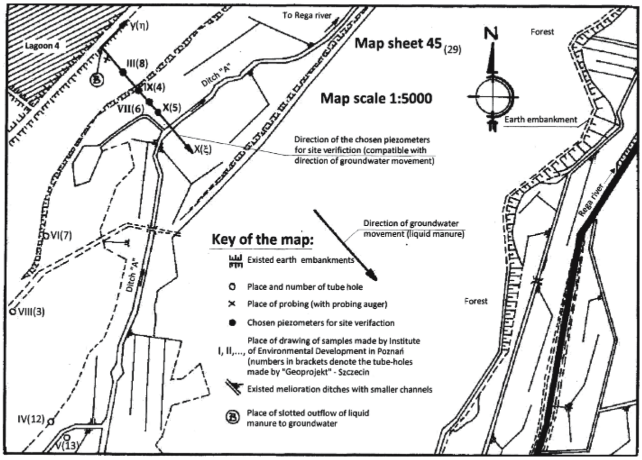

Fig. 1. The illustrative map of the chosen site (piezometers) adopted for numerical calculations and practical verification of the presented here transport models (equations) (Aniszewski [2])

the samples collected directly in the considered lagoon 4 and treated as the initial C_o concentrations. In relation to the real (observed) conditions of the source of the liquid manure influx into the natural aquifer, the infinitesimal width of the geotextile slotted vertical cracking was assumed in the further analysis (for the numerical solution and calculations of the presented transport equations).

In the further analysis, taking into consideration the relatively short chosen ground medium $L \approx 105\ m$, the lack of fluid sources (positive) and sinks (negative) for species k_o in equation (1) was also assumed ($q_S C_S^{k_0} = 0$). This measured distance L was the total length between the liquid manure leakage source in the lagoon 4 and the last chosen piezometer X (5) – see Fig. 1 and Tables 1 and 2). The term ($q_S C_S^{k_0}$) (classified as areally distributed or point sinks/sources) may be viewed as the “internal” sink/source term which represents the change in solute mass storage caused by the change in transient groundwater storage. It does not cause mass to leave or enter the model domain. In the governing equation (1) the species index k_o, for the simplicity of presented in the further parts equations, is also dropped.

So, finally, taking into consideration all the above-mentioned assumptions, the simplified forms of equation (1) in 2D domains were presented in the further parts of this paper in relation to the x (ξ) and y (η) axes (see equations 3, 8, 14 and 18).

General description of contaminant transport in groundwater without adsorption process

Dropping, for chloride and sulfate indicators, both the adsorption process (R = 1) and the biological and chemical reactions in the ground ($\sum R_n = 0$), the most simplified well-known and reduced 2D form of equation (1) is the following (Spitz and Moreno [9], Zheng and Wang [14], Chiang [3], Zhang *et al.* [13]):

$$\frac{\partial C}{\partial t} + u_x \frac{\partial C}{\partial x} = D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} \tag{2}$$

where:

u_x	the component of the so called pore groundwater velocity in pore space along the x axis [$m \cdot s^{-1}$],
D_x, D_y	the components of the longitudinal and transverse dispersion coefficients along the x and y axes that depend on the longitudinal and transverse dispersivities (α_L, α_T), [$m^2 \cdot s^{-1}$],
(x, y)	the Cartesian co-ordinates of the assumed reference system [m].

In equation (2) the adsorption process was neglected theoretically in the first stage of numerical calculations in relation to analyzed chloride and sulfate indicators. So, for such an assumption, the well-known retardation factor (R), resulting from the adsorption process, equals to 1 (as $R = 1 + \frac{\rho}{m} \cdot \frac{\partial S}{\partial C} = 1.00$). The explanation of the parameters appearing in this retardation factor (R) are given in the further part of this paper after equation 7).

In the further analysis the adsorption process, proceeding always in the natural groundwater streams, is taken also into consideration (see also eqs. 8, 14 and 18 with the adsorption terms). The dimensionless form of equation (2) is written bellow:

$$\frac{\partial C^*}{\partial \tau} + \frac{\partial C^*}{\partial \xi} = D_x^* \frac{\partial^2 C^*}{\partial \xi^2} + D_y^* \frac{\partial^2 C^*}{\partial \eta^2} \tag{3}$$

in which the following auxiliary dimensionless parameters were taken into account:

$$\frac{x}{L} = \xi, \quad \frac{y}{L} = \eta, \quad \frac{C}{C_o} = C^*, \quad \frac{u_x t}{L} = \tau, \quad \frac{D_x}{u_x L} = D_x^*, \quad \frac{D_y}{u_x L} = D_y^* \tag{4}$$

where:

L	the measured distance from the source of the contaminant outflow (injection) to the last cross-section (piezometer) in the chosen ground [m]. This measured distance (L) is treated as the known length of the solution area in the numerical solution (calculations) of the transport equations (3), (8), (14) and (18) ($L \approx 105$ m, see also Tables 1 and 2),
C_o	the initial measured contaminant concentrations in the source of the outflow (injection) into the chosen natural aquifer [$g \cdot m^{-3}$], along the vertical slot with assumed infinitesimal width of this slot.These concentrations (C_o) are treated as the known initial ones in the numerical solution (calculations) of the transport equations (3), (8), (14) and (18).

The exemplary initial numerical C_o concentration values for the chloride and sulfate indicators are given in the further part of this paper for the analyzed measurement series of May 1982. So, taking into account the above assumptions for numerical solution of equations (3), (8), (14) and (18) the initial and boundary dimensionless conditions were adopted in the form:

initial condition:

$$\begin{aligned} &C^{*}(0 \langle\, \xi \le \infty, 0 \langle\, \eta \le \infty, \tau = 0) = 0 \\ &C^{*}(\xi = 0, \eta = 0, \tau = 0) = 1 \end{aligned} \tag{5}$$

boundary conditions:

$$\begin{aligned} &C^{*}(\xi = 0, 0 \langle\, \eta \le \infty, \tau \,\rangle\, 0) = 0 \\ &C^{*}(\xi = 0, \eta = 0, \tau \,\rangle\, 0) = 1 \\ &C^{*}(\xi \to \infty, 0 \langle\, \eta \le \infty, \tau \rangle\, 0) = 0 \end{aligned} \tag{6}$$

These conditions as equations (5) and (6) are related to the considered semi-confined plane of groundwater flow. In this analysis, taking into account the symmetry, the area of flow was considered for ($0 < \xi \le \infty$) and ($0 < \eta \le \infty$). In further numerical calculations the asterisk symbol for the concentration values was neglected ($C^* = C$).

General description of contaminant transport in groundwater with adsorption process

Taking into consideration the adsorption process ($R \neq 1$) and neglecting the biological and chemical reactions in the ground ($\sum R_n = 0$), the simplified well-known and reduced 2D form of equation (1) can be expressed as follows (Spitz and Moreno [9], Seidel-Morgenstern [8], Chiang [3], Zhang *et al.* [13]):

$$\frac{\partial C}{\partial t}\left(1 + \frac{\rho}{m}\frac{\partial S}{\partial C}\right) + u_x \frac{\partial C}{\partial x} = D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} \tag{7}$$

where:

S	the mass of the solute species adsorbed on the grounds per unit bulk dry mass of the porous medium (in the local equilibrium conditions) [–],
ρ	the bulk density of the porous medium [$g \cdot m^{-3}$],
m	the effective porosity of the porous medium [–],
$[1 + (\rho / m) \cdot (\partial S / \partial C)]$	the constant in time retardation factor ($R \neq 1$) resulting from sorption process [–] (Chiang [3]).

The dimensionless form of equation (7) is the following:

$$\frac{\partial C^*}{\partial \tau} + A_1^{\,*} \frac{\partial C^*}{\partial \xi} = A_1^{\,*} \cdot D_x^* \frac{\partial^2 C^*}{\partial \xi^2} + A_1^{\,*} \cdot D_y^* \frac{\partial^2 C^*}{\partial \eta^2} \tag{8}$$

in which the following auxiliary dimensionless parameters were taken into account:

$$\begin{aligned} &\frac{x}{L} = \xi; \quad \frac{y}{L} = \eta; \quad \frac{C}{C_o} = C^*; \quad \frac{u_x t}{L} = \tau; \quad \frac{D_x}{u_x L} = D_x^* \\ &\frac{D_y}{u_x L} = D_y^*; \quad \frac{m}{m + \rho\, N\, K\, C_o^{\,(N-1)}\; C^{*(N-1)}} = A_1^{\,*} \end{aligned} \tag{9}$$

In the further analysis for description of adsorption term in equation (8) the Freundlich non-linear isotherm ($S = K \cdot C^N$) was assumed (Aniszewski [1], Aniszewski [2], Seidel-Morgenstern [8]).

The numerical values of the Freundlich K and N parameters were calculated based on the updated author's laboratory research for all the chosen indicators just in relation to the analyzed here later measurement series of May 1982. According to this presented here measurement series of May 1982, the exemplary and updated numerical values of the K and N parameters are: $K = 0.4091 \cdot m^3 \cdot g^{-1}$ and $N = 0.6103$ for chloride indicator and $K = 1.2648\ m^3 \cdot g^{-1}$ and $N = 0.8368$ for sulfate indicator, respectively. These numerical values of the K and N parameters presented in this paper differ from the K and N ones related to the earlier presented measurement series of November 1981 (given in Aniszewski [1] and Aniszewski [2]). One can say that in all cases they are smaller values than those given in the earlier presented measurement series of November 1981. So, the general equation describing dimensionless retardation factor (R) for all the indicators adopted here takes the form (Seidel-Morgenstern [8]):

$$R = 1 + \frac{\rho}{m} \cdot \frac{\partial S}{\partial C} = 1 + \frac{\rho}{m} \cdot N \cdot K \cdot C^{(N-1)} \tag{10}$$

It should also be noted that the retardation factor (R) is a constant value in time for the constant porosity of natural aquifers but depends on the concentration values. Numerical values of the calculated retardation factors based on equation (10) (treated as average values R_a) for all the chosen indicators are given in the explanation under Table 1 (in footnote 2). According to the presented here later measurement series of May 1982, the exemplary initial measured contaminant concentration in the source of the outflow into the chosen natural aquifer (as the lagoon 4 with liquid manure) are: $C_o \approx 298.0\ g \cdot m^{-3}$ for chlorides and $C_o \approx 394.0\ g \cdot m^{-3}$ for sulfates, respectively.

These above-mentioned initial numerical C_o concentration values differ from the C_o values related to the earlier measurement series of November 1981 (given in Aniszewski [1] and Aniszewski [2]). One can say that in all cases they are greater values than those given in the earlier presented measurement series of November 1981.

The dimensionless initial measured contaminant concentrations in relation to the initial measured contaminant ones in the lagoon 4 with liquid manure, for all the presented here contaminants, are given also in Table 1 as footnote a (as the values equal to 1.00). All the measured concentration data (C_o and $C_{\max m}$) related to the analyzed here later measurement series of May 1982 were described in an unpublished report entitled "Results of physico-chemical and bacteriological analyses of water samples together with documentation and conclusions resulted from these analyses for agricultural complex "Redło" in Redło nearby Świdwin". This report was prepared by the Institute of Environmental Development in Poznań (in Polish) and it may be obtained from the author.

It should also be noticed that the measured chloride and sulfate concentrations ($C^*_{\max m}$) between the particular piezometers are burdened with certain measurement errors. For this reason the variation between them does not have a character of an exponential curve (same as for the numerically calculated concentrations both with and without the adsorption process for all the presented indicators). So, these measured concentrations for the exemplary two indicators were not combined between the particular piezometers in Fig. 2. The other measured concentration values ($C^*_{\max m}$) for all the remaining analyzed here contaminants in relation to the other later measurement series of May 1982 may be obtained from the author.

General description of contaminant transport in groundwater with biodegradation/biological denitrification and adsorption processes

Taking into consideration both the adsorption process ($R \neq 1$) and the proceeding biological and chemical reactions in the ground (as biodegradation/biological denitrification process) ($\sum R_n \neq 0$), the well-known and reduced 2D form of equation (1) can be expressed as follows (Spitz and Moreno [9], Zheng and Wang [14], Chiang [3], Joekar-Niasar *et al.* [5], Zhang *et al.* [13]):

$$\frac{\partial C}{\partial t}\left(1+\frac{\rho}{m}\frac{\partial S}{\partial C}\right)+u_x\frac{\partial C}{\partial x}=D_x\frac{\partial^2 C}{\partial x^2}+D_y\frac{\partial^2 C}{\partial y^2}-\sum R_n \tag{11}$$

where:

$\sum R_n$ the function describing in this case biodegradation/biological denitrification process being considered in the chosen ground [$g \cdot m^{-3} \cdot s^{-1}$].

The ($\sum R_n$) function for biodegradation/biological denitrification process is the following (Spitz and Moreno [9], Zheng and Wang [14], Chiang [3], Joekar-Niasar *et al.* [5], Zhang *et al.* [13]):

$$\sum R_n=-\rho\frac{\partial S}{\partial t}-k_1 mC-\rho\, k_2 S \tag{12}$$

where:

k_1 the first-order reaction rate for the kinetically-controlled biodegradation process for the dissolved (aqueous) phase [s^{-1}],

k_2 the first-order reaction rate for the kinetically-controlled biodegradation process for the sorbed (solid) phase [s^{-1}].

However, in this analysis, for biodegradation process, the same parameter, k, was assumed for both the dissolved (aqueous) and the sorbed (solid) phases (with a possibility of certain differences between the values of this parameter in relation to the two above-mentioned phases). This above-mentioned remark can be noticed by Spitz and Moreno [9], Zheng and Wang [14], Chiang [3], Javadi and AL-Najjar [4], Weiss and Cozarelli [12], Joekar-Niasar *et al.* [5], Zhang *et al.* [13]. So, taking into consideration the above-mentioned remarks and substituting equation (12) into equation (11), equation (11) can be rearranged and written as:

$$\frac{\partial C}{\partial t}\left(1+\frac{\rho}{m}\frac{\partial S}{\partial C}\right)+u_x\frac{\partial C}{\partial x}=D_x\frac{\partial^2 C}{\partial x^2}+D_y\frac{\partial^2 C}{\partial y^2}-k\ (C-\frac{\rho\, S}{m}) \tag{13}$$

where:

k the first-order reaction rate for the kinetically-controlled biodegradation process (biological denitrification) for both the dissolved (aqueous) and the sorbed (solid) phases [s^{-1}] .

Based on the literature analysis, one can say that the nitrate biodegradation rate degree (biological transformation), proceeding in a natural groundwater, strongly depends on such physico-chemical parameters as: groundwater temperature (T), water reaction (pH) and oxidation-reduction potential called in short redox potential (Eh). Different, each time, values of these above-mentioned parameters (T, pH, Eh) existing in natural aquifers, strongly affect different numerical values of the biodegradation first-order rate constants (k_1 and k_2) in these aquifers (in relation to different moving contaminants).

The nitrate ions (NO_3^-) and BOD indicator (biochemical oxygen demand that can also be used for determining indirectly the concentration of substances susceptible to biodegradation process) were chosen in the present analysis (Javadi and AL-Najjar [4], Weiss and Cozarelli [12], Joekar-Niasar *et al.* [5]). Basing on the analyzed literature, in the case of nitrate biodegradation, one can rather speak of biological transformation (reaction), treated in a saturated zone mainly as biological denitrification.

More detailed explanations concerning the complex biodegradation process in a natural groundwater along with description of the physical and chemical parameters depending on this process are given by Spitz and Moreno [9], Zheng and Wang [14], Chiang [3], Javadi and AL-Najjar [4], Weiss and Cozzarelli [12], Kraft *et al.* [7], Joekar-Niasar *et al.* [5], Aniszewski [2], Zhang *et al.* [13].

The numerical optimum literature values of the chosen indicators in relation to biodegradation process/biological denitrification used in numerical calculations are: $k = 0.18 \times 10^{-5}$ s^{-1} for nitrates and $k = 0.67 \times 10^{-5}$ s^{-1} for BOD indicator, respectively. The above-mentioned numerical values, k, were adopted after detailed analysis of these parameters based on the unpublished Polish literature. This literature was taken in relation to both the chosen Polish (cold) climate and the ground located in the West Pomeranian Province of Poland analyzed here.The dimensionless form ofequation (13) is the following:

$$\frac{\partial C^*}{\partial \tau} + A_1^* \frac{\partial C^*}{\partial \xi} = A_1^* D_x^* \frac{\partial^2 C^*}{\partial \xi^2} + A_1^* D_y^* \frac{\partial^2 C^*}{\partial \eta^2} - k^* C^* (A_1^* + A_2^*) \tag{14}$$

in which the following auxiliary dimensionless parameters were taken into account:

$$\begin{gathered}
\frac{x}{L} = \xi, \ \frac{y}{L} = \eta, \ \frac{C}{C_o} = C^*, \ \frac{u_x t}{L} = \tau, \ \frac{D_x}{u_x L} = D_x^*, \ \frac{D_y}{u_x L} = D_y^* \\
k^* = k \ \frac{L}{u_x} = k \ t, \ \frac{m}{m + \rho N K C_o^{(N-1)} C^{*(N-1)}} = A_1^* \\
\frac{\rho K C_o^{(N-1)} C^{*(N-1)}}{m + \rho N K C_o^{(N-1)} C^{*(N-1)}} = A_2^*
\end{gathered} \tag{15}$$

General description of contaminant transport in groundwater with radioactive decay and adsorption processes

Taking into consideration both the adsorption process ($R \neq 1$) and the proceeding radioactive decay in the ground ($\sum R_n \neq 0$), the well-known and reduced 2D form of equation (1) can be expressed as equation (11) (Spitz and Moreno [9], Zheng and Wang [14], Chiang [3]). However, in this case, the ($\sum R_n$) function for radioactive decay can be expressed as follows (Spitz and Moreno [9], Zheng and Wang [14], Chiang [3], Zhang *et al.* [13]):

$$\sum R_n = -\rho \frac{\partial S}{\partial t} - \lambda_1 m C - \rho\, \lambda_2 S \tag{16}$$

where:

- λ_1 the first-order reaction rate for the radioactive decay for the dissolved (aqueous) phase [s^{-1}],
- λ_2 the first-order reaction rate for the radioactive decay for the sorbed (solid) phase [s^{-1}].

Assuming that, generally, if the reaction is radioactive decay, the first-order decay constant, λ, for the dissolved (aqueous) phase should be equal to such a constant for the sorbed (solid) phase. This above-mentioned remark can be noticed by Spitz and Moreno [9], Zheng and Wang [14], Chiang [3], Konikow *et al.* [6], Javadi and AL-Najjar [4], Zhang *et al.* [13]. So, taking into consideration the above-mentioned remark and substituting equation (16) into equation (11), equation (11) can be rearranged and written as:

$$\frac{\partial C}{\partial t} + u_x \frac{\partial C}{\partial x} = D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} - \frac{\rho}{m}\frac{\partial S}{\partial t} - \lambda\, (C - \frac{\rho\, S}{m}) \tag{17}$$

where:

- λ the first-order decay rate usually expressed as a half-life ($t_{1/2}$) for both the dissolved (aqueous) and the sorbed (solid) phases [s^{-1}].

The numerical calculations were carried out for the theoretical radionuclide taken from the literature (following Aniszewski [1]) with the first-order decay rate constant $\lambda \cong 0.01\ s^{-1}$ (for the relatively short half-life $t_{1/2} \cong 70\ s$) (see also text for given references – see Konikow *et al.* [6] and footnote 4 in Table 1). More detailed explanations concerning the radioactive decay in a natural groundwater for various radionuclides aregiven by Konikow *et al.* [6], Spitz and Moreno [9], Zheng and Wang [14], Javadi and AL-Najjar [4], Aniszewski [1], Zhang *et al.* [13]. The dimensionless form of equation (17) is the following:

$$\frac{\partial C^*}{\partial \tau} + A_1^* \frac{\partial C^*}{\partial \xi} = A_1^* \cdot D_x^* \frac{\partial^2 C^*}{\partial \xi^2} + + A_1^* \cdot D_y^* \frac{\partial^2 C^*}{\partial \eta^2} - \lambda^* \cdot C^* (A_1^* + A_2^*) \tag{18}$$

in which the following auxiliary dimensionless parameters were taken into account:

$$\frac{x}{L}=\xi,\ \frac{y}{L}=\eta,\ \frac{C}{C_o}=C^*,\ \frac{u_x t}{L}=\tau,\ \frac{D_x}{u_x L}=D_x^*,\ \frac{D_y}{u_x L}=D_y^*$$
$$\lambda^*=\lambda\cdot\frac{L}{u_x}=\lambda\cdot t,\ \frac{m}{m+\rho\cdot N\cdot K\cdot C_o^{(N-1)}\cdot C^{*(N-1)}}=A_1^* \tag{19}$$
$$\frac{\rho\cdot K\cdot C_o^{(N-1)}\cdot C^{*(N-1)}}{m+\rho\cdot N\cdot K\cdot C_o^{(N-1)}\cdot C^{*(N-1)}}=A_2^*$$

The numerical values of the calculated dimensionless and maximal (η = 0) concentrations ($C^*_{\max c} = C_{\max c}/C_o$) based on equations (3), (8), (14) and (18) are given in Table 1 and are referred to the appropriate footnotes in the previously chosen piezometers. However, the chosen only calculated dimensionless and maximal (η = 0) concentrations ($C^*_{\max c} = C_{\max c}/C_o$) based on equations (3) and (8) (without and with adsorption processes) are given also in Fig. 2 and are referred to the appropriate colours (see Fig. 2). The exemplary dimensionless measured chloride and sulfate concentrations ($C^*_{\max m} = C_{\max m}/C_o$) (marked as Δ symbol in brown for chlorides and as ● symbol in black for sulfates, respectively) are given also in Fig. 2 in relation to the later measurement series of May 1982. The remaining numerical values of both the calculated dimensionless concentrations ($C^*_{\max c}$) and the measured dimensionless ones ($C^*_{\max m}$) were not presented in Fig. 2, taking into consideration preservation of its legibility.

At the same time the numerical optimum values of all the remainingrequired parameters being considered in all the presented equations (3), (8), (14) and (18) (as updated parameterization of all these equations in relation to both the chosen contaminants and the considered ground medium) are the following:

- the parameters ($u_x = 1.05\times10^{-3}\,m/s$, $\rho = 1.71\,g/m^3$, m = 0.36) as the adopted real ground ones basing on unpublished technical reports (in Polish) – in relation to the measurement series of May 1982 analyzed here,
- the parameters [$D_x = 7.35\times10^{-3}\,m^2/s\ (\alpha_L = 7.0\,m)$, $D_y = 5.88\times10^{-3}\,m^2/s\ (\alpha_T = 0.56\,m)$] as the optimum dispersion ones calculated by the author of this paper.

The above-mentioned parameter values, related to the later measurement series of May 1982 analyzed here, differ from the parameter values related to the earlier measurement series of November 1981 (given in Aniszewski [1] and Aniszewski [2]). One can say that in all cases these parameter values are smaller values than those calculated in the earlier presented measurement series of November 1981. General comment concerning both all the final results of numerical calculations and the general conclusions resulting from these calculations is given in the further parts of this paper.

RESULTS AND DISCUSSION OF NUMERICAL CALCULATIONS

In the numerical calculations of the dimensionless maximum concentrations ($C^*_{\max c}$) for all the indicators chosen in this paper were carried out based on both the well-known

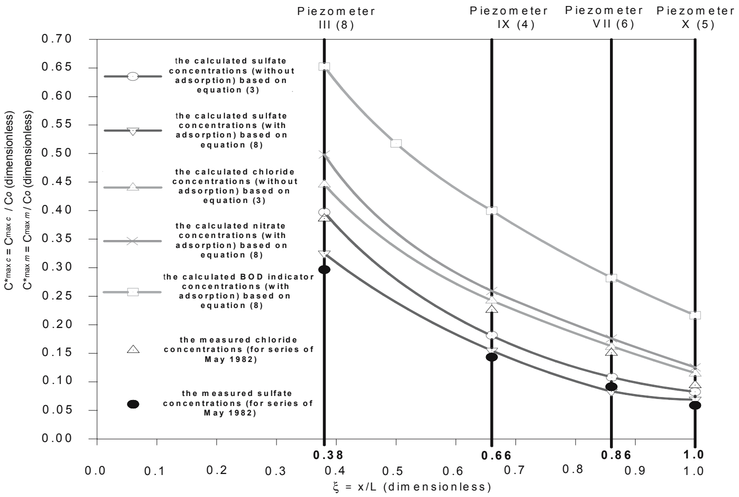

Fig. 2. Maximal values of the dimensionless numerically calculated concentrations ($C^*_{\max c}$) for all the analyzed indicators in the chosen earlier piezometers along with the exemplary dimensionless measured concentrations for chlorides and sulfates ($C^*_{\max m}$) in the chosen piezometers (in relation to the measurement series of May 1982).

"upwind" scheme (as "explicit" finite difference one that is described in detail, in, e.g, Szymkiewicz [10]) and the author's updated computational program „PCCS – 2.1". This author's program allows for obtaining the dimensionless values of the contaminant concentrations (without and with all the processes chosen here) in the range < 0, 1 >. However, the method of linearization of the presented here reduced equations (3), (8), (14) and (18) along with approximation of the first and second derivatives in all these equations were presented in detail, in, e.g, Aniszewski [1] and Aniszewski [2]. In the adopted numerical solution of equations (3), (8), (14) and (18) the values of dimensionless steps of the difference scheme grid (h^*, k^*) were determined in relation to the real range scale ($L \approx 105.0\ m$) of contamination transport in the previously chosen aquifer (Aniszewski [1] and Aniszewski [2]). The numerical values of dimensionless steps of the adopted difference scheme grids ($h^* = \Delta x / L \cong 0.01$, $k^* = \Delta y / L \cong 0.001$) were determined under the assumption that the numerical value of the Peclet number should not be larger than two ($Pe \leq 2$)

$$Pe = \frac{u_x \cdot \Delta x \ (\Delta y)}{D_x \ (D_y)} = \frac{u_x \cdot \Delta x \ (\Delta y)}{\alpha_L \cdot u_x \ (\alpha_T \cdot u_x)} = \frac{\Delta x \ (\Delta y)}{\alpha_L \ (\alpha_T)} \leq 2,$$

that is, the difference scheme grid should also be no larger than twice the dispersivities (α_L, α_T) as the characteristic length of heterogeneities of the ground systems (Szymkiewicz [10]). In practice, the Peclet number constraint is often relaxed outside the area of interest, where a lower predictive accuracy is acceptable. Such numerical Peclet number values lower than two ($Pe \leq 2$) minimize simultaneously the "numerical dispersion" and "artificial oscillations" in relation to equations (3), (8), (14) and (18), where the contaminant transport in ground is dominated not only by the advection process. For such an assumption, the well-known "upwind" scheme (as "explicit" finite difference scheme) is particularly suitable in numerical calculations (Szymkiewicz [10]).

In the further analysis, the numerical value of dimensionless time step of the adopted difference scheme grid ($w^* = u_x \cdot \Delta t / L \cong 0.01$) was also determined. This numerical value of time step minimizes both the so called "numerical dispersion" and "artificial oscillations". One can also say that this time step was determined under the assumption that the numerical value of the Courant number should not be larger than one ($C_a = u_x \cdot \Delta t / \Delta x \leq 1$) (Szymkiewicz [10]). In these numerical calculations (for the adopted dimensionless values of difference scheme grids), the important consistency, stability and convergence conditions were also preserved. These conditions minimize both the "numerical dispersion" and "artificial oscillations" in relation to all the above-mentioned equations describing particular processes (Szymkiewicz [10]). More details concerning the adopted "upwind" scheme are given in (Aniszewski [1] and Aniszewski [2]).

All the results of the presented here numerical calculations of the dimensionless concentration values ($C^*_{\max\ c}$) according to equations (3), (8), (14) and (18) in the previously chosen piezometers are given in Table 1. In this Table 1 are given also the exemplary dimensionless measured concentration values ($C^*_{\max\ m}$) for chlorides and sulfates. However, all the results as the standard errors of the numerical concentration calculations (in % and ‰) are given in Table 2 later also in the text and are the following:

- ➢ based on equations (3) and (8) (with and without the adsorption process in relation to the calculated contaminant concentrations with adsorption): from 2.9 to 8.8 for chlorides and from 14.1 to 19.3 for sulfates (as the maximal errors, see also Fig. 2) (values referred to footnote 1, in %). At the same time, one can say that all these above-mentioned maximal standard errors are different from the standard errors based on both equation (8) (with adsorption process) and the measured contaminant concentrations in relation to the measured contaminant ones in the previously chosen piezometers. The numerical values of the calculated earlier standard errors in relation to the measured contaminant concentrations are as follows: from 1.3 to 6.1 for chlorides and from 5.6 to 9.5 for sulfates (values in the parentheses referred to footnote 4, in %).

Additionally, it should be emphasized that the measured concentration values are lower compared to the calculated ones, for all the chosen here contaminants. This above-mentioned remark causes a greater margin of the safety for prognosis and simulation of concentration values calculated based on all the presented transport models (equations) (see Table 1). In opposite case practical using of all the presented transport models could be questionable for calculations of contaminant concentrations in ground systems.

The exemplary lower concentration values for chlorides and sulfates in relation to the calculated concentration values are also presented in Fig. 2 (the symbols of these indicators were given earlier in the text).

- ➢ based on equations (8) and (14) (with and without biodegradation process and with adsorption in both cases): from 0.8 to 10.8 for nitrates and from 2.0 to 4.7 for the BOD indicator (as the minimal errors) (values referred to footnote 2, in ‰),

- ➢ based on equations (8) and (18) (with and without radioactive decay and with adsorption in both cases): from 1.8 to 4.0 for the chosen radionuclide (values referred to footnote 3, in %) (see also text for references – Konikow *et al.* [6]).

The presented here both the numerical calculations of dimensionless concentration values (Table 1) and the standard errors (Table 2) confirmed also the importance (hierarchy) of the most important and chosen here processes. This confirmation is related to the concentration reduction values for all the moving contaminants in the analyzed ground (from sulfates as the highest reduction to nitrates and BOD indicator as the lowest one). It should be noted that the above-mentioned remarks confirmed also the earlier calculations in relation to the previously chosen measurement series of November 1981, presented in Aniszewski [1] and Aniszewski [2].

Additionally, it should be noted that all the measured concentration values from the presented here measurement series of May 1982 are greater than the measured concentration values in the earlier measurement series of November 1981 (given in Aniszewski [1] and Aniszewski [2]). It can show a gradual depletion in time of the adsorbing capacity in the presented here sandy aquifer with fine sand filling in relation to the adsorption process, as the process that causes the greatest concentration reduction values.

This fact is connected at the same time with decreasing in time the retardation factors (R) that depend on contaminant concentration values in ground systems (see equation 10 and remarks given earlier in the text). We can also say that these calculated retardation factors (R) will be gradually approaching the values $R \cong 1.00$ (for the total depletion of the adsorbing capacity of porous media). Simultaneously, it means that the S value, as the mass of the solute species adsorbed on the grounds per unit bulk dry mass of the porous medium, will be gradually approaching the zero value $S \cong 0$ (see equation 10 earlier in the text).

The lower numerical values of (R) (treated as average values R_a) are given in Table 1 as footnote 2 compared to the greater R_a values for the earlier measurement series of November 1981given in Aniszewski [1] and Aniszewski [2]. Nevertheless, to confirm all the above-mentioned remarks, it seems to be necessary to carry out further practical verifications of the presented author's numerical transport models (equations). These models should be related to other ground regions (with installed piezometers) with both the same or other climatic and the same or other ground conditions, compared to these conditions presented here (as another sets of parameters used in the transport models presented in this paper).

GENERAL CONCLUSIONS

1. Based on both all the new parameters and all the numerical calculations, given in this paper for the unpublished measurement series of May 1982, one can generally confirm:

- ➢ similar importance of all the chosen processes proceeding in groundwater, same like for the earlier presented measurement series of November 1981 (all the detailed conclusions concerning this importance are given in Aniszewski [1] and Aniszewski [2], hence neglected in this paper).

2. It can also be said that all the presented author's transport models in the chosen groundwater stream are a certain contribution and supplement in relation to the numerous more-or-less similar literature models (equations). It should also be noted that it is very hard to define concentration values based on the numerous literature models (equations), and then to compare them with the concentration values obtained with the author's models presented here. This is connected with both different climatic and ground conditions (as negative or positive charging – an "anionic" or "cationic" exchange of various natural ground media in relation to the solid phases – see also earlier in the text) and some other important factors, namely:

Table 1. Maximal dimensionless calculated values of the chosen contaminant concentrations ($C^*_{\max c}$) according to appropriate equations along with exemplary dimensionless measured concentrations ($C^*_{\max m}$) (for chlorides and sulfates in the chosen earlier piezometers for measurement series of May 1982)

Chosen contamination in relation to considered processes	Numbers of chosen piezometers with dimensionless and dimensional distances from the leakage source in lagoon 4 [total distance L to the last piezometer X (5) – *L ≈ 105.0 m*]			
	III (8) 0.38 x ≈ 40.0 m	IX (4) 0.66 x ≈ 70.0 m	VII (6) 0.86 x ≈ 90.0 m	X (5) 1.00 x (L) ≈ 105.0 m
Chlorides (NaCl) [adsorption process]	$0.4457^{1)}$ $0.4097^{2)}$ $1.00^{a)}$ $(C^*_{\max m} = 0.3862)$	$0.2425^{1)}$ $0.2283^{2)}$ $1.00^{a)}$ $(C^*_{\max m} = 0.2249)$	$0.1627^{1)}$ $0.1553^{2)}$ $1.00^{a)}$ $(C^*_{\max m} = 0.1531)$	$0.1057^{1)}$ $0.1027^{2)}$ $1.00^{a)}$ $(C^*_{\max m} = 0.1014)$
Sulfates (Na_2SO_4) [adsorption process]	$0.3879^{1)}$ $0.3250^{2)}$ $1.00^{a)}$ $(C^*_{\max m} = 0.2968)$	$0.1818^{1)}$ $0.1550^{2)}$ $1.00^{a)}$ $(C^*_{\max m} = 0.1435)$	$0.1122^{1)}$ $0.0975^{2)}$ $1.00^{a)}$ $(C^*_{\max m} = 0.0916)$	$0.0753^{1)}$ $0.0660^{2)}$ $1.00^{a)}$ $(C^*_{\max m} = 0.0625)$
Nitrates (NO_3^-) [biodegradation process]	$0.4995^{2)}$ $0.4934^{3)}$ $1.00^{a)}$	$0.2648^{2)}$ $0.2625^{3)}$ $1.00^{a)}$	$0.1678^{2)}$ $0.1667^{3)}$ $1.00^{a)}$	$0.1147^{2)}$ $0.1146^{3)}$ $1.00^{a)}$
BOD indicator [biodegradation process]	$0.6563^{2)}$ $0.6231^{3)}$ $1.00^{a)}$	$0.4010^{2)}$ $0.3882^{3)}$ $1.00^{a)}$	$0.2819^{2)}$ $0.2750^{3)}$ $1.00^{a)}$	$0.2131^{2)}$ $0.2056^{3)}$ $1.00^{a)}$
Chosen radionuclide [radioactive decay]	$0.3606^{2)}$ $0.3467^{4)}$ $1.00^{a)}$	$0.1760^{2)}$ $0.1705^{4)}$ $1.00^{a)}$	$0.1067^{2)}$ $0.1037^{4)}$ $1.00^{a)}$	$0.0701^{2)}$ $0.0689^{4)}$ $1.00^{a)}$

Explanations: $^{1)}$ MDC (maximal dimensionless concentrations $C^*_{\max c}$) acc. to eq. (3) without adsorption ($R = 1.00$ for chlorides and sulfates). $^{2)}$ MDC acc. to eq. (8) with adsorption ($R_a \approx 1.03$ for chlorides, $R_a \approx 2.11$ for sulfates, $R_a \approx 1.75$ both for nitrates and for BOD indicator – same as for nitrates and $R_a \approx 1.03$ for chosen radionuclide – same as for chlorides). $^{3)}$ MDC acc. to eq. (14) both with adsorption ($R_a \approx 1.82$ both for nitrates and for BOD indicator – same as for nitrates) and biodegradation ($k^* \approx 0.17$ for nitrates and $k^* \approx 0.62$ for BOD indicator). $^{4)}$ MDC acc. to eq. (18) with adsorption ($R_a \approx 1.03$ for chosen radionuclide – same as for chlorides) and with radioactive decay ($\lambda^* \approx \lambda \cdot t$) (as literature value of λ – see also text for references [6]). $^{a)}$ Initial dimensionless concentrations in relation to the initial measured ones in the lagoon 4 with liquid manure (for the presented here later measurement series of May 1982).

Table 2. Dimensionless calculated standard error values ($\Delta / C^*_{\max c}$) in relation to the numerically calculated concentrations along with the exemplary dimensionless standard error values ($\Delta / C^*_{\max m}$) in relation to measured concentrations (for chlorides and sulfates as footnote 4 in parentheses)

Chosen contamination in relation to considered processes	Numbers of chosen piezometers with dimensionless and dimensional distances from the leakage source in lagoon 4 [total distance L to the last piezometer X (5) – $L \approx 105.0\ m$]			
	III (8) 0.38 x ≈ 40.0 m	IX (4) 0.66 x ≈ 70.0 m	VII (6) 0.86 x ≈ 90.0 m	X (5) 1.00 x (L) ≈ 105.0 m
Chlorides (NaCl) [adsorption process]: $\Delta / C^*_{\max c}$ eq. (8) × 100% $\Delta = \vert C^*_{\max c}$ [eqs. (3) − (8)] $\vert$ $\Delta / C^*_{\max m}$ for footnote 4) in parentheses $\Delta = \vert C^*_{\max c}$ eq. (8) − $C^*_{\max m} \vert$	$8.8^{1)}$ $(6.1)^{4)}$	$6.2^{1)}$ $(1.5)^{4)}$	$4.8^{1)}$ $(1.4)^{4)}$	$2.9^{1)}$ $(1.3)^{4)}$
Sulfates (Na_2SO_4) [adsorption process]: $\Delta / C^*_{\max c}$ eq. (8) × 100% $\Delta = \vert C^*_{\max c}$ [eqs. (3) − (8)] $\vert$ $\Delta / C^*_{\max m}$ for footnote 4) in parentheses $\Delta = \vert C^*_{\max c}$ eq. (8) − $C^*_{\max m} \vert$	$19.3^{1)}$ $(9.5)^{4)}$	$17.3^{1)}$ $(8.0)^{4)}$	$15.1^{1)}$ $(6.4)^{4)}$	$14.1^{1)}$ $(5.6)^{4)}$
Nitrates (NO_3^-) [biodegradation process]: $\Delta / C^*_{\max c}$ eq. (14) × 1000 ‰ $\Delta = \vert C^*_{\max c}$ [eqs. (8) − (14)] $\vert$	$10.8^{2)}$	$8.7^{2)}$	$6.2^{2)}$	$0.8^{2)}$
BOD indicator [biodegradation process]: $\Delta / C^*_{\max c}$ eq. (14) × 1000 ‰ $\Delta = \vert C^*_{\max c}$ [eqs. (8) − (14)] $\vert$	$4.7^{2)}$	$3.3^{2)}$	$2.5^{2)}$	$2.0^{2)}$
Chosen radionuclide [radioactive decay]: $\Delta / C^*_{\max c}$ eq. (18) × 100% $\Delta = \vert C^*_{\max c}$ [eqs. (8) − (18)] $\vert$	$4.0^{3)}$	$3.2^{3)}$	$2.9^{3)}$	$1.8^{3)}$

Explanations: $^{1)}$ SE (standard errors) between MDC acc. to eqs. (3) and (8) with ($R_a \approx 1.03$) and without ($R = 1.00$) adsorption process for chlorides and with ($R_a \approx 2.11$) and without ($R = 1.00$) adsorption process for sulfates in [%] in relation to MDC acc. to eq. (8). $^{2)}$ SE between MDC acc. to eqs. (8) and (14) with ($k^* \approx 0.17$ for nitrates and $k^* \approx 0.62$ for BOD indicator) and without ($k^* = 0$) biodegradation (with adsorption $R_a \approx 1.75$ both for nitrates and for BOD indicator – same as for nitrates) in [‰] in relation to MDC acc. to eq. (14). $^{3)}$ SE between MDC acc. to eqs. (8) and (18) with ($\lambda^* \approx \lambda \cdot t$) (as literature value of λ – see also text for references [6]) and without ($\lambda = 0$) radioactive decay (with adsorption $R_a \approx 1.03$ for chosen radionuclide – same as for chlorides) in [%] in relation to MDC acc. to eq. (18). $^{4)}$ SE between MDC acc. to eq. (8) with ($R_a \approx 1.03$) adsorption process for chlorides and with ($R_a \approx 2.11$) adsorption process for sulfates in [%] in relation to the measured concentrations $C^*_{\max m}$ in the chosen piezometers.

- ➢ different scales (lengths) of contaminant propagation plumes used each time, with the necessity of determining geometric scale-depended similarity for the contaminant plumes (containing various micro- or macroscopic ground heterogeneities) (Joekar-Niasar *et al.* [5]),
- ➢ different selection or calculation of all the required parameters occurring in the equations presented here and in the literature, based on laboratory or field measurements (as various numerical values ranging over large intervals, also as concerns different climatic and ground conditions).

In the next turn all the dimensionless calculated standard error values ($\Delta / C^*_{\max c}$) in relation to the numerically calculated concentrations along with the exemplary dimensionless standard error values ($\Delta / C^*_{\max m}$) in relation to measured concentrations (for chlorides and sulfates as footnote 4 in parentheses) are given below in Table 2 in the previously chosen piezometers.

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REFERENCES

[1] Aniszewski, A. (2009). Mathematical modeling and practical verification of groundwater and contaminant transport in a chosen natural aquifer. *Acta Geophys*, 57, 435–453, DOI: 10.2478/s11600-008-4.

[2] Aniszewski, A. (2011). Particular application of a mathematical transport model incorporating sub-surface reactive pollutants. *Acta Geophys,* 59, 110−123, DOI: 10.2478/s11600-010-0040-7.

[3] Chiang, W-H. (2005). *3D-Groundwater modeling with PMWIN. A simulation system for modeling groundwater flow and pollution*. Heidelberg–New York: Springer, Verlag.

[4] Javadi, A.A., & AL-Najjar, M.M. (2007). Finite element modeling of contaminant transport in soils including the effect of chemical reactions. *Journal of Hazard. Mater,* 143, 690–701, DOI: 10.1016/j.jhazmat.2007.01.016.

[5] Joekar-Niasar, V., Ataie-Ashanti, B., & Sattari, Z. (2008). *Large scale modeling of nitrogen transformation in the unsaturated zone – A case study of Tehran City, Iran.* UK, London: Taylor & Francis Group, 169−179. DOI: 10.1201/9780203894569.ch 17.

[6] Konikow, L.F., Goode, D.J., & Hornberger, G.Z. (1996). *A three-dimensional method-of-characteristics solute-transport model (MOC3D*). USA, Virginia, Reston: U.S. Geological Survey, Water-Resources Investigations.

[7] Kraft, G.J., Browne, B.A., De Vita, W.M., & Mechenich D.J. (2008). *Agricultural pollutant penetration and steady state in thick aquifers*, Ground Water 46, 41−50, DOI: 10.1111/j.1745- 6584.2007.00378.

[8] Seidel-Morgenstern, A. (2004). Experimental determination of single solute and competitive adsorption isotherms. *Journal Chromatogr.* A 1037, (1–2), 255−272. DOI: 10.1016/j.chroma.2003.11.108.

[9] Spitz, K.H., & Moreno, J. (1996). *A practical guide to groundwater and solute transport modelling*, New York: John Wiley and Sons.

[10] Szymkiewicz, R. (2010). Numerical modelling in open channel hydraulics. *Water Sci. Technol. Library*, 83. DOI: 10.1007/978-90-481-3674-2.

[11] Taniguchi, M., & Holman, I.M. (2010). Groundwater response to changing climate. *CRC Press*. DOI: 10.1201/b10530-18.

[12] Weiss, J.V., & Cozzarelli, I.M. (2008). Biodegradation in contaminated aquifers: Incorporating microbal/molecular methods. *Ground Water*, 46. 305−322. DOI: 10.1111/j.1745-6584.2007.00409.x.

[13] Zhang, F., Yeh., G-Tsyh (George)., & Parker, J.C. (2012). *Groundwater reactive transport models*. Bentham, eBooks, DOI: 10.2174/97816080530631120101, eISBN: 978-1-60805-306-3

[14] Zheng, Ch., & Wang, P.P. (1996). *MT3DMS: A modular transport three-dimensional multispecies transport model for simulation of advection, dispersion, and chemical reactions of contaminants in groundwater systems; Documentation and user's guide*. Tuscaloosa: Dept. of Geol. Sci., University of Alabama, AL 35487, Contract Reports SERDP-99-1.

OPIS I WERYFIKACJA MODELI TRANSPORTU ZANIECZYSZCZEŃ W WODZIE GRUNTOWEJ (TEORIA I PRAKTYKA)

W artykule przedstawia się generalny przegląd 2D matematycznych modeli zarówno nieorganicznych, jak i organicznych zanieczyszczeń płynących w warstwie wodonośnej, biorąc pod uwagę najważniejsze procesy, jakie zachodzą w gruncie. Procesy te wpływają w różnym stopniu na wartości redukcji stężeń dla płynących w wodzie gruntowej zanieczyszczeń. W tej analizie wzięto pod uwagę następujące procesy: odwracalna nieliniowa fizyczna adsorpcja, chemiczne i biologiczne reakcje (jako biodegradacja/biologiczna denitryfikacja) oraz rozpad promieniotwórczy (dla płynących radionuklidów). W oparciu o prezentowane 2D modele transportu zanieczyszczeń było możliwe przeprowadzenie numerycznych obliczeń bezwymiarowych wartości stężeń z uwzględnieniem i bez uwzględnienia wszystkich wybranych procesów w odniesieniu zarówno do wybranego naturalnego gruntu (piezometrów) jak i do wybranych zanieczyszczeń. W pracy było również możliwe porównanie wszystkich obliczonych numerycznie wartości stężeń do wartości pomierzonych (w wybranych wcześniej piezometrach) w odniesieniu zarówno do nowej niepublikowanej wcześniej serii pomiarowej z maja 1982 jak i do nowego zestawu parametrów wykorzystanego w tych 2D modelach transportu zanieczyszczeń (jako praktyczna weryfikacja tych modeli).