

# Impact of ground adsorption capacity on the change in chemical composition of groundwater

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**Abstract:** Demonstrating the impact of time-dependent ground adsorption capacity on the change in chemical composition of groundwater is an important issue in understanding the groundwater mass transport process. Commonly used parameters characterizing ground adsorption capacity ( $R_a$ ,  $u_x^* = u_x/R_a$ ,  $\Delta C_{\max}^*$ ) were analyzed in this work to demonstrate time-varying values of this capacity for a chosen type of ground. Analysis of values of the selected parameters showed a gradual time decline in ground adsorption capacity as well as a gradual increase of groundwater contamination. This gradual increase in groundwater contamination over time is also important in practice. It implies the necessity to use more and more advanced (expensive) methods of water treatment in groundwater intakes.

## Introduction

Pollution transport in any type of ground is a complex issue due to the need of taking into account many physical and climatic factors in a given climatic zone in which this transport takes place (Chiang 2005, Taniguchi and Holman 2010). To describe this transport mathematical models have been successfully used for many years (Chalfen 2012, Chiang 2005, Kolditz et al. 2016, Morway et al. 2013, Szymański and Janowska 2016, Zhang and Fang 2016, Zheng and Wang 1996). For such models, tools for assessing groundwater quality without the need for expensive field research (“in situ”) are convenient. As a rule, in pollution transport mathematical models the most important physicochemical and biochemical processes occurring in the ground are described, such as: advection, dispersion, adsorption, biological or chemical reactions (biodegradation/denitrification) or the process of radioactive decay (Chalfen 2012, Chiang 2005, Kolditz et al. 2016, Morway et al. 2013, Szymański and Janowska 2016, Zhang and Fang 2016, Zheng and Wang 1996). It can also be said that mathematical description of all these processes is very difficult due to the lack of accurate methods of measuring the ongoing metabolism of these processes in the ground (Fang et al. 2012). This remark refers in particular to complex biochemical processes occurring in the ground (Fang et al. 2012, Morway et al. 2013, Zheng and Wang 1996). It can be observed that the greatest reduction in pollutants' concentration in groundwater is caused by the adsorption process (treated as a variable in time, ground adsorption capacity) (Chalfen 2012, Chiang 2005, Kolditz et al. 2016, Morway et al. 2013, Szymański and Janowska 2016, Zhang and Fang 2016, Zheng and Wang 1996).

The study of literature shows that time-dependent adsorption capacity of the ground is widely analyzed in relation to various types of grounds as well as various contaminants (Chalfen 2012,

Chiang 2005, Morway et al. 2013, Szymański and Janowska 2016, Zhang and Fang 2016, Zheng and Wang 1996). It can be noticed that in the case of a long period of time in which a pollutant flows in aquifer the ground adsorption capacity can gradually become depleted. This means that at some moment of time (at so called final time), a ground will no longer be able to adsorb flowing pollutants and concentrations of these pollutants will be the highest (Kowal et al. 1990, Seidel-Morgenstern 2004). In this research, the concentrations of chlorides and sulfates in a groundwater have been measured in some fixed points for flow times shorter than the final times corresponding to these points. For shorter flow times there is only a partial decline in ground adsorption capacity which implies lower concentrations of pollutants in groundwater as compared to the highest concentrations for the final time.

Ground adsorption capacity is determined in this work as a property of reversible physical process often described by means of adsorption isotherms. In such models, the state of equilibrium in exchange of given ions at the boundary between pollutant flowing in a liquid phase (as adsorbate) and those adsorbed on surface of solid phase (as adsorbent) is assumed. The adsorption isotherm models are described mathematically by means of linear or non-linear isotherms (Kowal et al. 1990, Seidel-Morgenstern 2004). Parameters of adsorption models depend on type of pollutants flowing in groundwater, physical features of ground as well as climatic conditions constituting climatic zone (Kowal et al. 1990, Seidel-Morgenstern 2004, Szymański and Janowska 2016, Zhang and Fang 2016, Zheng and Wang 1996).

Taking into account the above remarks, the first objective of this work was to demonstrate time declining ground adsorption capacity. The second objective of the work was to demonstrate an increase in groundwater contamination as a consequence of time declining ground adsorption capacity. Both objectives have

been achieved by analyzing the results of numerical modelling, laboratory experiment and field studies. The accomplishment of the assumed objectives indicates some novelty in an approach for addressing an impact of time-varying ground adsorption capacity on change in chemical composition of groundwater. The selection and assessment of three parameters characterizing ground adsorption capacity there may also be considered as a novelty in quantifying non-stationarity of this adsorption process.

### **Selection and description of parameters characterizing ground adsorption capacity**

In the work, three time-varying parameters characterizing ground adsorption capacity have been chosen for chlorides and sulfates:

- retardation factor ( $R_a$ ) (Table 3),
- average velocity of ions dissolved in flowing groundwater ( $u_x^*$ ) taking into account adsorption process ( $u_x^* = u_x/R_a$ ) (Table 1),
- difference ( $\Delta C_{\max}^*$ ) between calculated ( $C_{\max c}^*$ ) and measured ( $C_{\max m}^*$ ) concentrations (Table 4).

The retardation factor ( $R_a$ ) defines how many times average ions' velocity of chlorides or sulfates ( $u_x^*$ ) dissolved in flowing groundwater is smaller (retarded) as compared to average velocity ( $u_x$ ) of a groundwater.

It should be noted that values of concentrations ( $C_{\max c}^*$ ) calculated from equation (1) implicitly contain parameters ( $K$  and  $N$ ) of non-linear adsorption isotherm adopted in the analysis.

However, in addition to the adsorption process the measured concentrations ( $C_{\max m}^*$ ) (given in Table 4) may also take into account other processes autogenously occurring in ground referred to in the introduction to this work. It should also be emphasized that the parameter ( $\Delta C_{\max}^*$ ) has not been the subject of literature analysis so far in terms of using it for describing ground adsorption capacity.

### **Description of field measurements along with the results of calculations of hydraulic and ground parameters for a selected type of ground and interpretation of the results**

In 1981–1982, while designing a ground lagoon for slurry, the design office “Geoprojekt” in Szczecin carried out a field research to determine (“in situ”) hydraulic and ground parameters of the real aquifer (Szczecin 1982). Slurry was brought to this lagoon from the existing pig farm “Redło” near Świdwin in West Pomeranian Province. At the same time, based on the observation of this lagoon by the user, it

was recognized that it was a source of leakage of slurry to the tested aquifer. This caused a significant deterioration the in groundwater quality within the aquifer along the direction from this lagoon to the river Rega. Therefore, in order to monitor the deteriorating quality of groundwater, “Geoprojekt” has installed a line of four piezometers along the direction of groundwater flow in the aquifer at irregular intervals on a total length of ca. 105.0 meters. The individual distances between the four piezometers from the lagoon's edge with their markings and numbering are given in Table 4.

Average slope of a free groundwater table in the entire aquifer ( $I$ ) was determined from slope values of a groundwater between four installed piezometers. To determine average value coefficient of hydraulic conductivity ( $k$ ) for the entire aquifer both so called “the Kamiński tube” and additionally some empirical formulas were applied for samples taken from individual piezometers. Thus, average velocity ( $u_x$ ) of a groundwater was determined, based on the dependence ( $u_x = I \cdot k/m$ ) using also the effective ground porosity ( $m$ ).

For ground samples taken from the piezometers, the average value of the bulk density of ground ( $\rho$ ) was determined in laboratory tests (by means of a VICAT-HDT type apparatus suitable for measuring this type of density). Whereas average value of the effective porosity ( $m$ ) of the ground was determined using the volume-weight method. The calculated average values of the above parameters ( $u_x$ ,  $\rho$ ,  $m$ ) are given in Table 1 for three measurement series made.

Table 1 presents the values of average ions' velocity of chlorides and sulfates ( $u_x^*$ ) being considered as well as values of average velocity ( $u_x$ ) of a groundwater. The values of retardation coefficients ( $R_a$ ) defining average ions' velocity ( $u_x^*$ ) were calculated on the basis of laboratory tests carried out by the author and described in the further section of this work in Table 3.

A more detailed description of the field tests measurements (“in situ”) and calculations of the above parameters made by “Geoprojekt” together with a map of this area can be found in the technical report made available to the author of this work (Szczecin 1982).

Interpreting the values of average ions' velocity of chlorides and sulfates ( $u_x^*$ ) a gradual increase of this velocity can be observed in three consecutive measurement series. The increase in average ions' velocity ( $u_x^*$ ) indicates a gradual time decline in ground adsorption capacity for chlorides and sulfates.

In addition, on the basis of ground samples, it can be also assumed that the aquifer is a homogeneous and isotropic. It consists mainly of fine-grain sands with only a small admixture of medium and coarse sands.

**Table 1.** Assumed and calculated hydraulic as well as ground parameters in analyzed ground (fine grained sand) for three measurement series (Szczecin 1982)

Measurement series	November 1981 (Aniszewski 2009)	May 1982 (Aniszewski 2013)	October 1982 (Aniszewski 2017)
Average velocity of a groundwater $u_x$ [ $\text{m} \cdot \text{s}^{-1}$ ]:			
– without adsorption ( $u_x$ ) ( $R_a = 1.00$ ) [Szczecin 1982]	$1.14 \cdot 10^{-3}$	$1.14 \cdot 10^{-3}$	$1.14 \cdot 10^{-3}$
– velocity of ions ( $u_x^* = u_x/R_a$ ) ( $R_a \neq 1.00$ ) (chlorides)	$1.07 \cdot 10^{-3}$	$1.11 \cdot 10^{-3}$	$1.13 \cdot 10^{-3}$
– velocity of ions ( $u_x^* = u_x/R_a$ ) ( $R_a \neq 1.00$ ) (sulfates)	$0.52 \cdot 10^{-3}$	$0.54 \cdot 10^{-3}$	$0.56 \cdot 10^{-3}$
Average bulk density of the ground $\rho$ [ $\text{g} \cdot \text{m}^{-3}$ ]	1.71	1.71	1.71
Average effective porosity of the ground $m$ [–]	0.37	0.37	0.37

### Assessment of longitudinal and transverse dispersion coefficients ( $D_x$ , $D_y$ ) and interpretation of the results

Values of longitudinal and transverse dispersion coefficients ( $D_x$ ,  $D_y$ ) were calculated for chlorides and sulfates. To calculate these coefficients, known relationships  $D_x = (u_x \cdot \alpha_L)$  and  $D_y = (u_y \cdot \alpha_T)$  were used. The effect of small molecular diffusion in a ground ( $D_M$ ) was omitted (Chalfen 2012, Chiang 2005, Kowal et al. 1990). For the laminar flow which occurs especially in a sandy ground the turbulent diffusion process can also be omitted (Chalfen 2012, Chiang 2005, Zhang and Fang 2016, Zheng and Wang 1996).

Based on the literature analysis (Chalfen 2012, Chiang 2005, Kowal et al. 1990) for the three measurement series the following values of longitudinal ( $\alpha_L$ ) and transverse ( $\alpha_T$ ) of the ground dispersivity were adopted (Table 2). As evidenced by the literature, the values of the ground transverse ( $\alpha_T$ ) dispersivity should be in the range of  $\alpha_T = (0.05 \div 0.30) \cdot (\alpha_L)$ . The values of ground longitudinal dispersivity ( $\alpha_L$ ) depend on the scale (length) of the spread of chlorides and sulfates in a ground. On the other hand, these values depend also on time evolution of dispersion process in ground (Chalfen 2012, Chiang 2005, Zhang and Fang 2016, Zheng and Wang 1996). All of the foregoing parameters ( $D_x$ ,  $D_y$ ,  $\alpha_L$ ,  $\alpha_T$ ) are given in Table 2 for three measurement series made.

For the observed decreasing values of dispersion coefficients ( $D_x$ ,  $D_y$ ) the following explanation can be given. The suspensions and colloids flowing along with a groundwater cause gradual filling in pores between grains thus changing structure of the pores. As a result of this filling, the space for spreading of pollutants in this ground is gradually narrowing causing gradual decrease in the values of dispersion coefficients ( $D_x$ ,  $D_y$ ). Decreasing numerical values of dispersion coefficients given in Table 2 confirm the above explanation.

### Description of laboratory tests and calculations for non-linear adsorption parameters ( $K$ , $N$ ) and retardation coefficients ( $R_a$ ) and interpretation of the results

To describe the adsorption term in equation (1) a non-linear Freundlich isotherm ( $S = K \cdot C^N$ ) was adopted in this work (Kowal et al. 1990, Seidel-Morgenstern 2004, Szymański and Janowska 2016, Zhang and Fang 2016, Zheng and Wang 1996). On the basis of laboratory tests it was possible to determine the values of non-linear adsorption parameters ( $K$ ,  $N$ ) for the assumed isotherm and then calculate the values of retardation coefficients ( $R_a$ ). As shown in the relevant type of literature, this isotherm

is particularly useful in relation to the theory of volume filling of micro-pores between the grains of any ground (as adsorbent) with a monolayer system of molecules (Kowal et al. 1990, Seidel-Morgenstern 2004). In addition, this isotherm is easy to apply due to simple mathematical formula (Kowal et al. 1990, Seidel-Morgenstern 2004). Therefore, taking into account the above remarks, this monolayered Freundlich isotherm was adopted at the work. The parameter ( $S$ ) in the Freundlich isotherm determines the mass of adsorbed pollutants per unit of dry mass of ground (under local equilibrium conditions) ( $mg \cdot g^{-1}$ ). The numerical values of the adsorption parameters ( $K$  and  $N$ ) for chlorides and sulfates in the three measurement series were determined based on the author's laboratory tests.

In laboratory tests, mass of ions adsorbed in the ground samples was determined in relation to the mass of these samples under static conditions (without a flow of groundwater) as a "batch" type study. Thirty samples of the ground (in the form of fine-grain sand samples) were used: fifteen for chlorides and fifteen for sulfates as two groups of individual samples. The mass of samples ( $m_o$ ) was in the range from 300 to 1000 g. All these samples of the ground were then mixed within a constant volume ( $V$ ) of solutions of sodium chloride and sodium sulfate ( $NaCl$ ,  $Na_2SO_4$ ) ( $V = 1.2 l = 1200 dm^3$ ) using respectively thirty different initial concentrations ( $C_i$ ) in the range from 200.0 to 450.0  $g \cdot m^{-3}$ . After mixing a solution over sufficiently long time ( $t_m$ ) ( $t_m = ca. 24 hours$ ) in equilibrium conditions, final concentrations of chlorides and sulfates in the solutions of the test samples ( $C$ ) were reached. The final concentrations in the test samples ( $C$ ) were from 199.7 to 448.8  $g \cdot m^{-3}$  for chlorides and from 198.9 to 446.5  $g \cdot m^{-3}$  for sulfates. Using the values of the foregoing parameters ( $C_i$ ), ( $C$ ), ( $V$ ) and ( $m_o$ ), the parameter values ( $S$ ) were calculated as the mass ratio of adsorbed pollutants in a given sample ( $mg$ ) to the mass of this sample ( $g$ ) [ $S = (C_i - C) \cdot V / m_o$ ].

Finally, on the basis of the determined values ( $S$  and  $C$ ), Freundlich non-linear isotherms functions ( $S = K \cdot C^N$ ) were specified for the tested indicators, together with the determination of the numerical values of parameters ( $K$  and  $N$ ). Having the parameters  $K$  and  $N$ , the numerical values of dimensionless retardation coefficients ( $R_a$ ) [ $R_a = 1 + \frac{\rho}{m} \cdot N \cdot K \cdot C^{(N-1)}$ ] were calculated. All the parameters ( $K$ ,  $N$ ,  $R_a$ ) are given in Table 3 for consecutive three series of measurements.

From laboratory tests carried out, one can notice different adsorption capacities of pollutants in the ground samples – higher for sulfates and lower for chlorides. This is evidenced

**Table 2.** Assumed and calculated dispersion parameters for selected pollutants (chlorides and sulfates) in analyzed ground for three measurement series (Aniszewski 2009, 2013, 2017, Chalfen 2012)

Measurement series		November 1981 (Aniszewski 2009)	May 1982 (Aniszewski 2013)	October 1982 (Aniszewski 2017)
Chlorides (NaCl) Sulfates (Na <sub>2</sub> SO <sub>4</sub> )	Coefficient of longitudinal dispersion $D_x$ [ $m^2 \cdot s^{-1}$ ]: [ $D_x = (u_x/R_a) \cdot \alpha_L$ ] (chlorides) [ $D_x = (u_x/R_a) \cdot \alpha_L$ ] (sulfates)	7.91 · 10 <sup>-3</sup> 3.84 · 10 <sup>-3</sup>	7.21 · 10 <sup>-3</sup> 3.51 · 10 <sup>-3</sup>	7.03 · 10 <sup>-3</sup> 3.48 · 10 <sup>-3</sup>
	Coefficient of transverse dispersion $D_y$ [ $m^2 \cdot s^{-1}$ ]: [ $D_y = (u_y/R_a) \cdot \alpha_T$ ] (chlorides) [ $D_y = (u_y/R_a) \cdot \alpha_T$ ] (sulfates)	6.31 · 10 <sup>-4</sup> 3.07 · 10 <sup>-4</sup>	6.11 · 10 <sup>-4</sup> 2.97 · 10 <sup>-4</sup>	5.88 · 10 <sup>-4</sup> 2.91 · 10 <sup>-4</sup>
	Constant of longitudinal dispersivity $\alpha_L$ [m]	7.39	6.50	6.22
	Constant of transverse dispersivity $\alpha_T$ [m]	0.59	0.55	0.52



by higher values of adsorbed pollutants for sulfates: from 1.1 to 3.5 g·m<sup>-3</sup> and, correspondingly, by lower values for chlorides: from 0.3 to 1.2 g·m<sup>-3</sup>.

Also numerical values of parameters ( $K$ ,  $N$ ,  $R_a$ ) can provide evidence of their gradual time decrease for the three measurement series. It may also be observed that gradual decrease in the numerical values of retardation coefficients ( $R_a$ ) indicates a gradual decline in the ground adsorption capacity. Hence, for this ground one can expect a complete depletion of this ground adsorption capacity for final time and consequently value of retardation coefficient ( $R_a = 1.00$ ). Obviously, for the case of ( $R_a = 1.00$ ) transport of pollutants in ground can be described by equation (1), in which the adsorption term is omitted. This case refers to chlorides for the last measurement series of October 1982, when the value of the retardation coefficient was  $R_a = 1.01 \approx 1.00$ . It can therefore be assessed that in the case of chlorides the final time is about one-year (as the time between the measurements of the first and the last series).

However, referring to sulfates the calculated value of the retardation coefficient ( $R_a = 2.04 \neq 1.00$ ) does not allow to infer about completed depletion of the ground adsorption capacity from the last series of measurements of October 1982. In the case of sulfates a total depletion of the ground adsorption capacity requires a much longer period of time than one-year. This shows that the time of a complete depletion of the adsorption capacity of a given ground definitely depends on the type of pollutant flowing in a groundwater.

#### Calculated concentrations, values of differences between calculated and measured concentrations and interpretation of the results

Subsequently, in the work, the values of dimensionless calculated concentrations ( $C_{\max c}^*$ ) were determined for chlorides and sulfates flowing in the aquifer. To calculate these concentrations, a simplified 2D equation of pollutant transport in the ground (1) and the “PCCS – 2.1” computer program developed by the author were used. In the equation (1) only the processes of advection, two-dimensional dispersion and non-linear adsorption were considered, omitting the biochemical reactions that may occur in a ground:

$$\frac{\partial C^*}{\partial \tau} + A_1^* \frac{\partial C^*}{\partial \xi} = A_1^* \cdot D_x^* \frac{\partial^2 C^*}{\partial \xi^2} + A_1^* \cdot D_y^* \frac{\partial^2 C^*}{\partial \eta^2} \quad (1)$$

taking into account the following dimensionless (auxiliary) parameters:

$$\frac{x}{L} = \xi; \quad \frac{y}{L} = \eta; \quad \frac{C}{C_o} = C^*; \quad \frac{u_x t}{L} = \tau; \quad \frac{D_x}{u_x L} = D_x^* \quad (2)$$

$$\frac{D_y}{u_x L} = D_y^*; \quad \frac{m}{m + \rho N K C_o^{(N-1)} C^{*(N-1)}} = A_1^*$$

where:

- $C$  concentrations of pollutants in a flowing groundwater (in local equilibrium conditions) [g·m<sup>-3</sup>],
- $D_x, D_y$  components of the longitudinal and transversal dispersion coefficients along the x, y axes, which depend on constants of dispersivity ( $\alpha_L, \alpha_T$ ), along the x, y axes (Table 2) [m<sup>2</sup>·s<sup>-1</sup>] respectively,
- $x, y$  Cartesian coordinates [m],
- $u_x$  component of average velocity of a groundwater (without adsorption process), along x axis (Table 1) [m·s<sup>-1</sup>] respectively,
- $t$  time [s],
- $m$  dimensionless effective ground porosity (Table 1) [-],
- $\rho$  bulk density of ground (Table 1) [g·m<sup>-3</sup>],
- $K$  a constant of non-linear Freundlich isotherm (Table 3) [m<sup>3</sup>·g<sup>-1</sup>],
- $N$  a constant dimensionless exponent of non-linear Freundlich isotherm (Table 3) [-],
- $L$  parameter representing the real measured distance from source of pollutants (lagoon with slurry) to the last cross-section [as piezometer X (5)] ( $L = 105.0$  m – see Table 4) [m] (Szczecin 1982),
- $C_o$  parameter representing the initial measured concentration of pollutants in source of their outflow (lagoon with slurry) to ground tested ( $C_o = 300.0$  g·m<sup>-3</sup> for chlorides and  $C_o = 400.0$  g·m<sup>-3</sup> for sulfates) [g·m<sup>-3</sup>] (Szczecin 1982).

The calculated and measured values of parameters ( $u_x, \rho, m, D_x, D_y, K, N, C_o, L$ ) were used to determine auxiliary and dimensionless parameters in equation (2).

Subsequently values of concentrations ( $C_{\max c}^*$ ) based on equation (1) were calculated using the author’s “PCCS – 2.1” program. In this program an “explicit” finite differential scheme (as “upwind” scheme) was used for the assumed initial and boundary conditions (Szymkiewicz 2010, Aniszewski 2009).

In these calculations, the conditions of consistency, stability and convergence to adopted differential scheme were also preserved (Szymkiewicz 2010). Simultaneously, in numerical

**Table 3.** Calculated adsorption parameters for selected pollutants (chlorides and sulfates) in analyzed ground for adopted non-linear Freundlich isotherm and for three measurement series (Aniszewski 2009, 2013, 2017)

Measurement series		November 1981 (Aniszewski 2009)	May 1982 (Aniszewski 2013)	October 1982 (Aniszewski 2017)
Chlorides (NaCl)	Coefficient of retardation $R_a$ [-]	1.06	1.03	1.01
	Constant of Freundlich isotherm $K$ [m <sup>3</sup> ·g <sup>-1</sup> ]	0.4132	0.4091	0.3098
	Constant exponent of Freundlich isotherm $N$ [-]	0.6122	0.6103	0.4978
Sulfates (Na <sub>2</sub> SO <sub>4</sub> )	Coefficient of retardation $R_a$ [-]	2.18	2.11	2.04
	Constant of Freundlich isotherm $K$ [m <sup>3</sup> ·g <sup>-1</sup> ]	1.2854	1.2648	1.0645
	Constant exponent of Freundlich isotherm $N$ [-]	0.8479	0.8368	0.7269

calculations discretization steps of the differential scheme were respected criterion values of Peclet and Courant numbers ( $Pe \leq 2$  and  $C_a \leq 1$ ). For such values the adopted scheme does not generate “numerical” dispersion nor artificial oscillations in numerical solutions of equation (1) (Szymkiewicz 2010).

The calculated values of concentrations ( $C^*_{\max c}$ ) are given in Table 4 (with upper index 1 for chlorides and 2 for sulfates, respectively – see explanations under this table). Also measured values of concentrations ( $C^*_{\max m}$ ) are given in Table 4 (with upper index 3 for chlorides and 4 for sulfates, respectively – see explanations under this table). Measured concentrations ( $C^*_{\max m}$ ) refer to the initial values of concentrations ( $C_o$ ) for chlorides

and sulfates in the lagoon with slurry ( $C^*_{\max m} = C^*_{\max m}/C_o$ ) ( $C_o = 300.0 \text{ g}\cdot\text{m}^{-3}$  for chlorides and  $C_o = 400.0 \text{ g}\cdot\text{m}^{-3}$  for sulfates) (Szczecin 1982). The calculated values of parameter ( $\Delta C^*_{\max}$ ) (as differences of calculated and measured concentrations) are also given in Table 4 (with the upper index 5 for chlorides and 6 for sulfates, respectively – see explanations under this table).

Measured values of concentrations ( $C^*_{\max m}$ ) as well as initial values ( $C_o$ ) were determined based on the field studies performed by the Institute of Environmental Development in Poznań. Description of the field studies both for the three measurement series and selected indicators are presented in the technical report (Szczecin 1982).

**Table 4.** Calculated maximum values of differences ( $\Delta C^*_{\max}$ ) between the calculated ( $\Delta C^*_{\max c}$ ) and measured ( $\Delta C^*_{\max m}$ ) concentration values for selected pollutants (chlorides and sulfates) and for three measurement series (Aniszewski 2009, 2013, 2017)

Type of pollution			Chlorides (NaCl)			Sulfates (Na <sub>2</sub> SO <sub>4</sub> )		
Analyzed concentrations			( $C^*_{\max c}$ ) according to (1) 1)[CDMC]	( $C^*_{\max m}$ ) according to [Szczecin 1982] 3)[MDMC]	( $\Delta C^*_{\max}$ ) 5)[CMD]	( $C^*_{\max c}$ ) according to (1) 2)[CDMC]	( $C^*_{\max m}$ ) according to [Szczecin 1982] 4)[MDMC]	( $\Delta C^*_{\max}$ ) 6)[CMD]
Measurement series: November 1981	The number of piezometers selected with distances from the source of the pollution leak (lagoon with slurry)	III (8) $\xi \approx 0.38$ $x \approx 40 \text{ m}$	0.4035 <sup>1)</sup>	0.3716 <sup>3)</sup>	0.0319 <sup>5)</sup>	0.3246 <sup>2)</sup>	0.2802 <sup>4)</sup>	0.0444 <sup>6)</sup>
		IX (4) $\xi \approx 0.66$ $x \approx 70 \text{ m}$	0.2383 <sup>1)</sup>	0.2172 <sup>3)</sup>	0.0211 <sup>5)</sup>	0.1543 <sup>2)</sup>	0.1338 <sup>4)</sup>	0.0205 <sup>6)</sup>
		VII (6) $\xi \approx 0.86$ $x \approx 90 \text{ m}$	0.1545 <sup>1)</sup>	0.1345 <sup>3)</sup>	0.0200 <sup>5)</sup>	0.0972 <sup>2)</sup>	0.0821 <sup>4)</sup>	0.0151 <sup>6)</sup>
		X (5) $\xi \approx 1.00$ $x \approx 105 \text{ m}$	0.0910 <sup>1)</sup>	0.0742 <sup>3)</sup>	0.0168 <sup>5)</sup>	0.0564 <sup>2)</sup>	0.0407 <sup>4)</sup>	0.0157 <sup>6)</sup>
Measurement series: May 1982	The number of piezometers selected with distances from the source of the pollution leak (lagoon with slurry)	III (8) $\xi \approx 0.38$ $x \approx 40 \text{ m}$	0.4097 <sup>1)</sup>	0.3862 <sup>3)</sup>	0.0235 <sup>5)</sup>	0.3250 <sup>2)</sup>	0.2968 <sup>4)</sup>	0.0282 <sup>6)</sup>
		IX (4) $\xi \approx 0.66$ $x \approx 70 \text{ m}$	0.2388 <sup>1)</sup>	0.2252 <sup>3)</sup>	0.0136 <sup>5)</sup>	0.1550 <sup>2)</sup>	0.1435 <sup>4)</sup>	0.0115 <sup>6)</sup>
		VII (6) $\xi \approx 0.86$ $x \approx 90 \text{ m}$	0.1553 <sup>1)</sup>	0.1392 <sup>3)</sup>	0.0161 <sup>5)</sup>	0.0975 <sup>2)</sup>	0.0916 <sup>4)</sup>	0.0059 <sup>6)</sup>
		X (5) $\xi \approx 1.00$ $x \approx 105 \text{ m}$	0.1027 <sup>1)</sup>	0.0902 <sup>3)</sup>	0.0125 <sup>5)</sup>	0.0671 <sup>2)</sup>	0.0625 <sup>4)</sup>	0.0046 <sup>6)</sup>
Measurement series: October 1982	The number of piezometers selected with distances from the source of the pollution leak (lagoon with slurry)	III (8) $\xi \approx 0.38$ $x \approx 40 \text{ m}$	0.4176 <sup>1)</sup>	0.2990 <sup>3)</sup>	0.0186 <sup>5)</sup>	0.3256 <sup>2)</sup>	0.3048 <sup>4)</sup>	0.0208 <sup>6)</sup>
		IX (4) $\xi \approx 0.66$ $x \approx 70 \text{ m}$	0.2399 <sup>1)</sup>	0.2287 <sup>3)</sup>	0.0112 <sup>5)</sup>	0.1562 <sup>2)</sup>	0.1489 <sup>4)</sup>	0.0073 <sup>6)</sup>
		VII (6) $\xi \approx 0.86$ $x \approx 90 \text{ m}$	0.1628 <sup>1)</sup>	0.1494 <sup>3)</sup>	0.0134 <sup>5)</sup>	0.0982 <sup>2)</sup>	0.0944 <sup>4)</sup>	0.0038 <sup>6)</sup>
		X (5) $\xi \approx 1.00$ $x \approx 105 \text{ m}$	0.1172 <sup>1)</sup>	0.1065 <sup>3)</sup>	0.0107 <sup>5)</sup>	0.0782 <sup>2)</sup>	0.0759 <sup>4)</sup>	0.0023 <sup>6)</sup>

**Explanations:** 1)[CDMC] (calculated dimensionless maximum concentrations) ( $C^*_{\max c}$ ) according to equation (1) (with adsorption) for chlorides in three measurement series, 2)[CDMC] ( $C^*_{\max c}$ ) according to equation (1) (with adsorption) for sulfates in three measurement series, 3)[MDMC] (measured dimensionless maximum concentrations) ( $C^*_{\max m} = c_{\max m}/C_o$ ) ( $C_o = 300.0 \text{ g}\cdot\text{m}^{-3}$ ) for chlorides in three measurement series according to (Szczecin 1982), 4)[MDMC] ( $C^*_{\max m} = c_{\max m}/C_o$ ) ( $C_o = 400.0 \text{ g}\cdot\text{m}^{-3}$ ) for sulfates in three measurement series according to (Szczecin 1982), 5)[CMD] (calculated maximum differences) ( $\Delta C^*_{\max}$ ) for chlorides in three measurement series, 6)[CMD] ( $\Delta C^*_{\max}$ ) for sulfates in three measurement series.

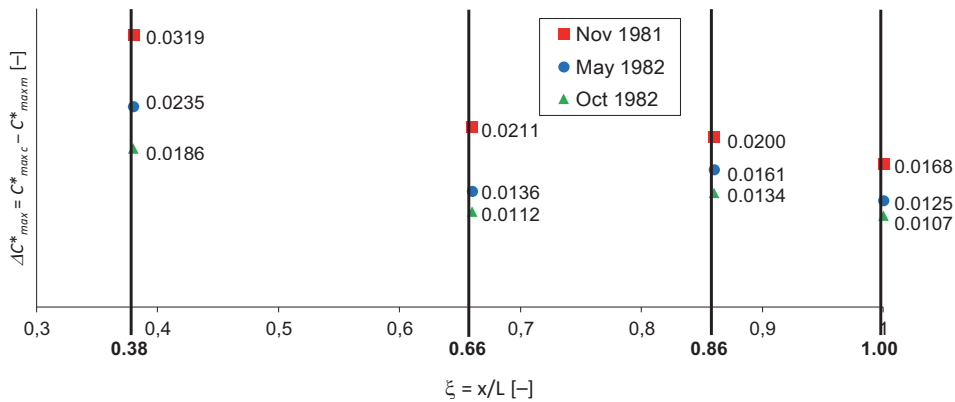
Values ( $\Delta C^*_{\max}$ ) given in Table 4 show their gradual time decrease, starting from the first series (November 1981 – as the highest value) to the last series (October 1982 – as the lowest value). A similar tendency can also be observed for the time-varying values of the differences of concentrations ( $\Delta C^*_{\max}$ ) between particular series of measurements in the corresponding measurement cross-sections. On the basis of the calculated difference values of concentration ( $\Delta C^*_{\max}$ ), one can therefore infer on the highest adsorption capacity of ground in the first measurement series (November 1981). The lowest ground adsorption capacity occurred for the last series of measurements (October 1982). This regularity is also confirmed by the lowest measured values of concentrations ( $C^*_{\max m}$ ) in the November 1981 measurement series and by the highest measured values of concentrations that occurred in the last series of October 1982 (Table 4). As can also be seen from Table 4, the values of the measured concentrations ( $C^*_{\max m}$ ) for chlorides and sulfates in all the three measurement series are smaller than the values of the calculated concentrations ( $C^*_{\max c}$ ). Such low values of the measured concentrations could have been caused by: high homogeneity of aquifer and fine-grained type of ground (Szczecin 1982).

Graphical results of dimensionless values of differences of concentrations ( $\Delta C^*_{\max}$ ) for chlorides are given below in Fig. 1 and for sulfates in Fig. 2 (respectively in the following colors:

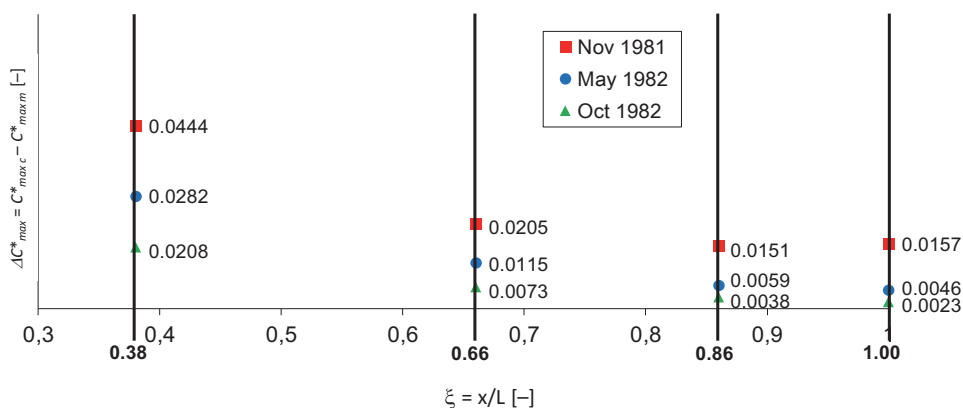
red for the series of November 1981; blue for the series of May 1982 and green for the series of October 1982).

### Final conclusions

1. Values of three parameters assessed in the paper ( $R_a$ ,  $u_x^* = u_x/R_a$  and  $\Delta C^*_{\max}$ ) characterizing ground adsorption capacity indicate a gradual time decline of this capacity.
2. A decline in ground adsorption capacity evokes a gradual increase of groundwater contamination (as the change in chemical composition of groundwater). Time increase in pollutant concentrations in consecutive measurement series confirms the above regularity (see Table 4).
3. Impact of time declining ground adsorption capacity on the increase in groundwater pollution has important practical consequences. It can be ascertain that in addition to many agricultural and industrial factors that affect the deterioration of the chemical composition of groundwater, one should also take into account time decrease of ground adsorption capacity (Rak et al. 2013, Zimoch et al. 2015). This is an important message for institutions and people occupied with groundwater abstraction when planning or operating groundwater intakes. This is especially true when groundwater is to be used for human consumption as drinking water. For such a use there is the necessity to



**Fig. 1.** Dimensionless values of differences ( $\Delta C^*_{\max}$ ) between the calculated ( $C^*_{\max c}$ ) and measured ( $C^*_{\max m}$ ) of concentrations for chlorides in three measurement series (Aniszewski 2009, 2013, 2017)



**Fig. 2.** Dimensionless values of differences ( $\Delta C^*_{\max}$ ) between the calculated ( $C^*_{\max c}$ ) and measured ( $C^*_{\max m}$ ) of concentrations for sulfates in three measurement series (Aniszewski 2009, 2013, 2017)

apply most advanced water-treatment technologies bearing in mind that with the passage of time costs of the treatment processing may be continually increasing.

It should be noted that all the foregoing final conclusions refer only to pollutants selected for analysis (i.e. chlorides and sulfates), the selected ground type and climatic zone, and about one-year time period of pollutants inflow into a selected ground (Szczecin 1982).

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## Wpływ pojemności adsorpcyjnej gruntu na zmianę składu chemicznego wód podziemnych

**Streszczenie:** Wykazanie wpływu zależnej od czasu pojemności adsorpcyjnej gruntu na zmianę składu chemicznego wód podziemnych jest ważnym zagadnieniem w zrozumieniu procesu transportu masy wód podziemnych. W niniejszej pracy przeanalizowano powszechnie stosowane parametry charakteryzujące pojemność adsorpcyjną gruntu ( $R_a$ ,  $u_x^* = u_x/R_a$ ,  $\Delta C_{\max}^*$ ), aby wykazać zmienne w czasie wartości tej pojemności. Dokładna analiza wartości liczbowych wybranych parametrów wykazała spadkową w czasie tendencję pojemności adsorpcyjnej gruntu, a także stopniowy wzrost zanieczyszczenia wód gruntowych. Ten stopniowy w czasie wzrost zanieczyszczenia wód gruntowych jest również ważny w praktyce. Wiąże się bowiem z koniecznością stosowania coraz bardziej zaawansowanych (kosztownych) metod uzdatniania wód podziemnych pobieranych z ujęć.