

## EXPERIMENTAL RESEARCHES CONCERNING A POLLUTED AQUIFER DECONTAMINATION

Mihaela Amalia DIMINESCU<sup>1</sup>, Anca Marina MARINOV<sup>23</sup>

*The presence and transport of contaminants in the groundwater is a more than widely recognized threat to the human health and environment. In order to better understand the miscible pollutants removal mechanisms from a shallow groundwater, a series of laboratory studies have been carried out looking at the pollutant concentration during a decontamination experiment. We will consider the water flow and the dispersion of a pollutant into a homogenous, isotropic, unconfined aquifer bounded by two lakes whose levels and qualities determine the flow in the aquifer and the pollutant's sources. Experimental data are compared to the numerical solutions of dispersion equation. A retardation factor of the dispersion process is obtained by an optimization procedure and the resulting factor is used to compute the decontamination efficiency.*

**Keywords:** groundwater, pollution, decontamination, dispersion, unconfined aquifer, retardation.

### 1. Introduction

Groundwater systems play an essential role in meeting the ever-increasing world demand for water.

Proper management of groundwater systems should therefore be a very important matter of concern, not only to ensure that water will be available in adequate quantity and quality to satisfy demands, but also to guarantee that this would be done in an optimal manner.

In this paper we analyze the influence of a lake or stream on the water quality of an unconfined, neighboring aquifer, considering the fate of a miscible pollutant. Due to the interconnections between streams and aquifers, stream pollution may influence aquifer pollution and conversely. A stream is a boundary condition in piezometric head for hydraulic model and in pollution concentration and flux for the groundwater pollution model. These concentration conditions are the outputs of a stream-pollution model.

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<sup>1</sup> Lecturer, Power Engineering Department, University POLITEHNICA of Bucharest, Romania,  
e-mail: mihaela.diminescu@yahoo.com

<sup>2</sup> Professor, Power Engineering Department, University POLITEHNICA of Bucharest, Romania,  
e-mail:ancamarinov@gmail.com

Many theoretical and numerical approaches [1], [2], consider the flow and mass transport in unconfined aquifers, and the methods to calibrate the resulted prediction models. Usually the diffusivity equation for the aquifer gives the hydraulic heads, necessary to calculate the velocities and the dispersion equation gives the concentration variation in space and time. The resulted model is called a “coupled model”. VISUAL MODFLOW [2] is one of the famous programs solving such types of problems.

The difficulties of model calibration will increase with the number of model's parameters.

We developed a simple, robust model to predict the pollutant concentration in an unconfined aquifer [3], [4] and calibrated it using experimental data. Two experiments (pollution and decontamination) will provide data for model calibration, taking in account the adsorption and desorption processes.

## 2. Mass Transport Model of Pollutants throughout an Isotropic, Unconfined Aquifer

Solutes dissolved in groundwater are subject to a number of different processes through which they can move and disperse in the porous medium, can be sorbed onto the surfaces of the mineral grains of the aquifer, sorbed by organic carbon that might be present in the aquifer, undergo chemical precipitation, be subject to abiotic as well as biodegradation, and participate in oxidation-reduction reactions.

Sorption is the change of molecules and ions between the solid phase and the liquid phase, including both adsorption and desorption. Adsorption is the attachment of molecules and ions from the solute to the solid material, causing a decrease of concentration of the solute. As a result of sorption processes, some solutes will move much more slowly through the aquifer than the groundwater that is transporting them. This effect is called retardation.

Desorption is the release of molecules and ions from the solid phase to the solute. Clean water, flowing through a polluted aquifer (during decontamination) will transport the pollutant solution from the pores and will influence desorption process too. We intend to evaluate this phenomenon.

### 2.1 Dispersion equation

The form of the partial differential equation describing one – dimensional transport of a chemical constituent through a porous medium is [5], [6]:

$$\frac{\partial}{\partial x} \left( \theta D \frac{\partial C}{\partial x} - qC \right) = \frac{\partial}{\partial t} (\theta C + \rho_b S) + \mu_w \theta C + \mu_s \rho_b S - \gamma_w \theta - \gamma_s \rho_b \quad (1)$$

where:  $C$  is the solution's concentration [ $\text{ML}^{-3}$ ] (mass of solute per unit volume of fluid);  $S$  is the adsorbed concentration [ $\text{MM}^{-1}$ ];  $\theta$  is the volumetric moisture content [ $\text{L}^3\text{L}^{-3}$ ];  $D$  is the dispersion coefficient [ $\text{L}^2\text{T}^{-1}$ ];  $q$  is the volumetric flux [ $\text{LT}^{-1}$ ], (Darcy's velocity);  $\rho_b$  is the porous medium bulk density [ $\text{ML}^{-3}$ ];  $\mu_w$  is the rate constant for first-order decay in the liquid [ $\text{T}^{-1}$ ];  $\mu_s$  is the rate constant for first-order decay in the soil phase of the soil [ $\text{T}^{-1}$ ];  $\gamma_w$  is the rate constant for zero-order production in the liquid [ $\text{ML}^{-3}\text{T}^{-1}$ ];  $\gamma_s$  is the rate constant for zero-order production in the soil phase [ $\text{T}^{-1}$ ].

For a linear isotherm adsorption relationship, with a distribution coefficient  $K_d$ ,

$$S = K_d C, \quad (2)$$

the chemical transport equation (1) takes the form:

$$\begin{aligned} \frac{\partial}{\partial x} \left( \theta D \frac{\partial C}{\partial x} - U_x C \right) &= \frac{\partial}{\partial t} \left( \theta C \left( 1 + \frac{\rho_b K_d}{\theta} \right) \right) + \theta C \left( \mu_w + \frac{\mu_s \rho_b K_d}{\theta} \right) - \\ &- \theta \left( \gamma_w + \frac{\gamma_s \rho_b}{\theta} \right) \end{aligned} \quad (3)$$

We will consider the particular case with sorbtion and without any other reactions. If a retardation factor is defined as:

$$R = 1 + \frac{\rho_b K_d}{\theta}, \quad (4)$$

and the interstitial or pore – water velocity is:

$$v = \frac{U_x}{\theta}, \quad (5)$$

the equation (3) can be written:

$$\frac{\partial}{\partial x} \left( \theta D \frac{\partial C}{\partial x} - v \theta C \right) = \frac{\partial}{\partial t} (C \theta R). \quad (6)$$

The equation (6) is valid for unsaturated soil and for saturated one (aquifers). Usually for an aquifer (saturated porous medium) the effective porosity  $n_e$  is used instead of  $\theta$ , and  $v = U/n_e$ .

For a homogenous aquifer,  $n_e$  is constant, and for a constant retardation factor  $R$  the transport equation will be:

$$\frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} - v C \right) = R \frac{\partial C}{\partial t}. \quad (7)$$

Considering a dynamic dispersion regime [7], [8],

$$D = D_0 + \alpha |v| \approx \alpha |v|, \quad (8)$$

where  $\alpha$  is the dynamic dispersivity, in  $x$  direction,  $v$  is the interstitial average linear groundwater velocity, and  $D_0$  is the molecular effective diffusion coefficient.

Due to adsorption, a reactive solute will travel at a slower rate than the groundwater flow.

Equations (3) and (4) can be used to solve contamination environmental problems in soils (6) or in groundwater (7).

We will calibrate a coupled model describing groundwater flow in  $x$  direction and the transport of a miscible pollutant in an unconfined aquifer (Fig.1).

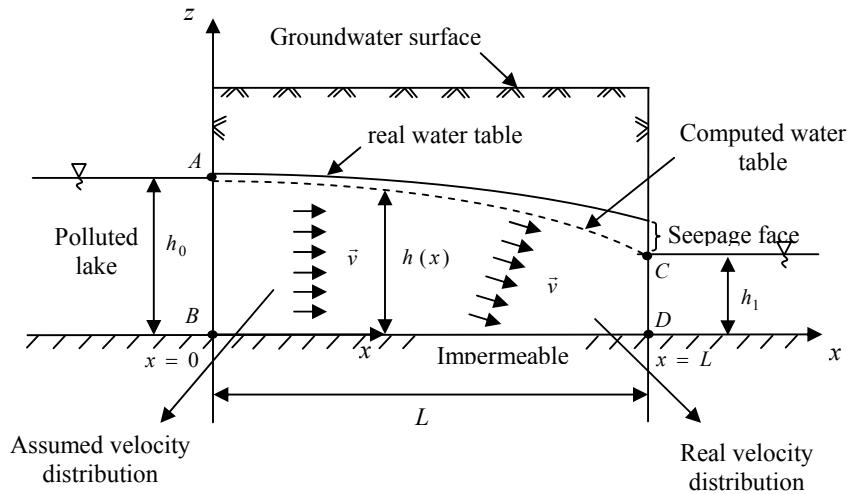


Fig. 1 Steady flow in an unconfined aquifer [9].

## 2.2. Hydraulic model

For a two dimensional homogenous, isotropic medium we assume Dupuit's hypothesis: *i1*) the velocity of the flow is proportional to the tangent of the hydraulic gradient instead of the sine, as defined Darcy's law; *i2*) the flow is horizontal and uniform everywhere in a vertical section (no flow in  $z$  direction), and calculate the discharge in the aquifer, the average linear groundwater velocity, and the thickness of the aquifer. The Darcy's velocity in the aquifer is

$$U_x = -K \frac{dh}{dx} \quad (9)$$

where  $K$  [ $L T^{-1}$ ] is the hydraulic conductivity,  $h$  [L] is the level of the water table above an impervious bed,  $x$  [L] is the direction of flow. The discharge per unit width, at any vertical section is:

$$q = -h \cdot K \frac{dh}{dx}. \quad (10)$$

The real interstitial water velocity in the groundwater is:

$$\vec{v} = \frac{\vec{U}}{n_e} \quad (11)$$

where  $n_e$  is the effective porosity of the aquifer.

Considering the aquifer from Fig. 1, the integral

$$\int_0^L q \, dx = \int_{h_0}^{h_1} -K h \, dh \quad (12)$$

gives the value of the discharge in the aquifer:

$$q = \frac{K}{2L} (h_0^2 - h_1^2), \quad (13)$$

$h_0$  and  $h_1$  are the water levels in the two water bodies neighboring the aquifer.

This result is known like Dupuit formula [2]. The thickness of the aquifer is

$$h(x) = \sqrt{h_0^2 - \frac{2q}{K} x}, \quad (14)$$

and the real interstitial velocity is:

$$v_x(x) = \frac{U_x(x)}{n_e} = \frac{q}{n_e \sqrt{h_0^2 - \frac{2q}{K} x}}. \quad (15)$$

The calculated velocity is constant for each vertical section, normal to flow, but change its value for different  $x$ . Excepting the boundaries AB and DC the results obtained with Dupuit's hypothesis are general accepted.

### 2.3. Numerical solution for dispersion equation

Our problem is to solve the advection-dispersion equation (7) for the unconfined aquifer from (Fig. 1), considering the variable velocity given by (15), and a dispersion coefficient (8) for a dynamic dispersion regime in the porous medium.

For boundaries conditions we consider the polluted lake (AB) having a  $C_0(t)$  concentration, and at the outflow lake (CD), an unknown concentration. The initial values of concentration in the aquifer are known.

We integrated the advection-dispersion equation (7) using an implicit numerical scheme described in [3], and used in [4]. The implicit approximations are unconditionally stable and convergent [1].

The one dimensional dispersion equation (7), with variable coefficients

$$\frac{\partial}{\partial x} \left( D(x) \frac{\partial C(x,t)}{\partial x} - v(x) C(x,t) \right) = R \frac{\partial C(x,t)}{\partial t}, \quad (16)$$

was approximated by finite differences, considering the initial and boundaries conditions, for two situations: a) pollution and b) decontamination of an unconfined aquifer.

For the pollution process the boundary conditions are:  
 $C(x = 0, t) = C_0 = \text{constant}$ , and  $\frac{\partial C(x,t)}{\partial x} = 0$ , for  $x = L, \dots$  (17)

and the initial condition  $C(x, t = 0) = 0$ . (18)

For the decontamination process the boundary conditions are

$$C(x = 0, t) = C_0(t), \frac{\partial C(x,t)}{\partial x} = 0, \text{ for } x = L, \quad (19)$$

and the initial condition:  $C(x, t = 0) = CI(x)$ . (20)

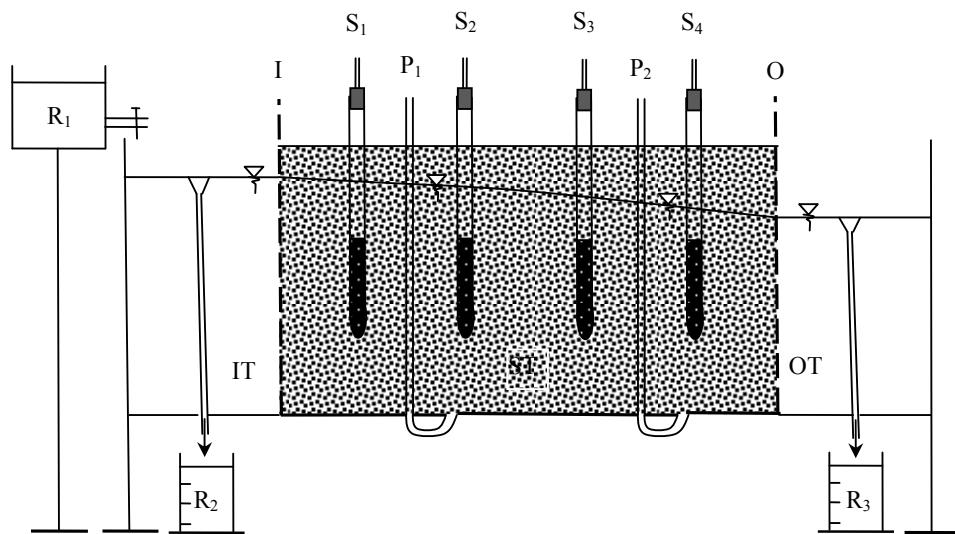
After model's calibration the numerical solutions are compared with measured concentrations in 4 "wells", at different moments "t". A retardation factor is calculated using an optimization procedure.

### 3. Experimental Set-up

The experimental bench is built to simulate, on a small scale, the hydrological principles of the groundwater flow and the pollutants behavior in saturated soils. The installation allows simple three dimensional flow situations to be set up quickly and measurements of piezometric levels taken at appropriate positions. The sand tank (fig. 1) is manufactured in glass and located in a steel frame which is designed for standing on a laboratory bench. A diffused water inlet (I) / outlet (O) with associated flow control level is installed at each end of the sand tank. By changing the position of water level in the inlet (IT) and outlet (OT) tanks, the desired water table can be established. Two toppings in the base of the tank are connected to a multi-tube piezometer ( $P_1, P_2$ ) on the side of the tank. The water levels in the piezometers indicate the water table position in the longitudinal groundwater profile. Four soil solution extracting tube ( $S_1, S_2, S_3, S_4$ ) are installed in the sand tank (ST). The discharge trough the groundwater can be volumetrically measured using calibrated reservoir R3 and can be modified controlling the levels position in the inlet and outlet tanks.



Fig. 2: Photograph of the experimental bench.

Fig. 3: The experimental bench.  $S_1, S_2, S_3, S_4$  – soil solution extracting tube;  $P_1, P_2$  – piezometric tube; IT – inlet water tank; OT – outlet water tank; ST – sand tank.

Groundwater can be polluted with contaminated water (from  $R_1$ ) having a known concentration. Soil solution is extracted at different time intervals with  $S_1$  –  $S_4$  tubes, using a vacuum pump. The hydro-dynamical and chemical behaviors of this groundwater are compared with the theoretical and numerical results. The water levels in piezometers indicate the water table position in the groundwater longitudinal profile.

The pollutant used for our experiment was a potassium permanganate,  $KMnO_4$ , solution with a concentration of 1507.29 mg/L. The intake reservoir was continuously filled with that solution during the pollution time (80 minutes). In the pollution experiment 34 samples were taken from six points, (the 2 tanks and 4 extraction wells).

For remediation (decontamination) the tank  $R_1$  was fed with clear water. During 167 minutes, 42 samples were taken in the same points mentioned above.

The samples were chemically analyzed to establish the potassium permanganate solute concentration, using titrimetric analysis [10], [11].

#### 4. Model calibration and results

For our experiment model calibration considers the dispersion equation (16) parameters  $D(x), v(x), R$  to have values closely evaluated comparatively with the real ones. The differences between the measured pollutant concentration and the numerical values obtained with the model have to be minimized.

For dispersion coefficient  $D = \alpha |v(x)|$ , as is recommended in [7], longitudinal dispersivity,  $\alpha = (1/10) \cdot L = 0.038 \text{ m}$ . The variable velocity is calculated with eq. (15). The effective porosity is 0.22 (experimental result), and the hydraulic conductivity is obtained from:  $q = \frac{K}{2L} (h_0^2 - h_1^2)$ . For a permanent regime we measured:  $h_0 = 0.33 \text{ m}$ ,  $h_1 = 0.297 \text{ m}$ ,  $L = 0.38 \text{ m}$ . The discharge  $q = (\Delta V / \Delta t) / \text{aquifer width} = (0.420 \cdot 10^{-3} \text{ m}^3 / 120 \text{ s}) / 0.29 \text{ m}$  - (volumetrically measured).

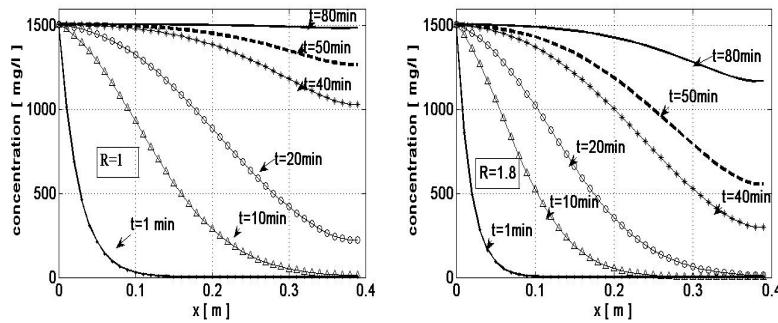


Fig.4. Concentration  $C(x,t,R)$ , along the aquifer, at different moments,  $t$ , during contamination. a)  $R=1$ , b)  $R=1.8$ .

The numerical values of pollutant concentrations obtained for two retardation factors  $R=1$  (no retardation) and  $R=1.8$  (Figure 4) are compared with the measured concentrations (for the extracted solution in S1:  $x_1=0.05 \text{ m}$ , in S2:  $x_2=0.15 \text{ cm}$ , S3:  $x_3=0.25 \text{ m}$ , S4:  $x_4=0.34 \text{ m}$ ). For  $R=1$ , big differences occur (See Fig. 5). Increasing  $R$ , the relative percentile errors between calculated and measured values decrease like in Fig. 6.

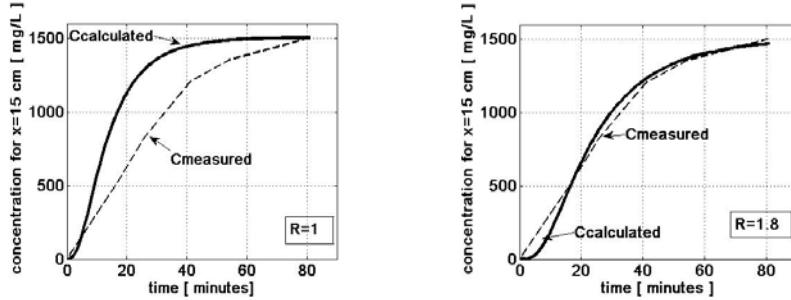


Fig.5. Time variation of concentration  $C(x,t)$ , at a distances  $x=15$  cm, for two values of retardation factor. Contamination case.

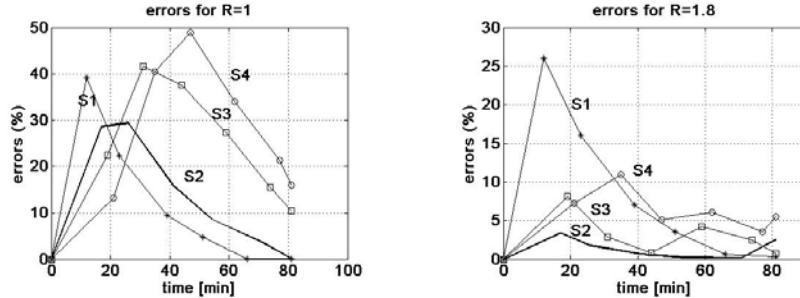


Fig. 6. Relative percentile errors, for two different retardation factors, between calculated and measured concentrations, in S1-S4 extraction tubes.

That result suggested us the idea to find a retardation factor value which minimize the sum of all the differences between the measured and numerical values. With an optimization procedure we find for retardation factor an optimal values  $R=1.78$ . That result will be used in the decontamination case too.

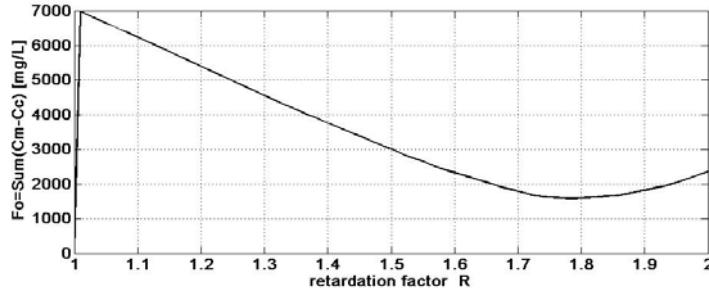


Fig. 7. Objective function minimization is obtained for retardation factor ( $R=1.78$ ).

For decontamination case, the same hydraulic regime is preserved, and the same parameters are used in the mathematical model. The condition on the inlet boundary  $C(x = 0, t) = C_0(t)$  is variable (see Fig. 8 a) corresponding to measured values in the inlet tank IT (Fig. 3). That tank, full of potassium permanganate solution for the contamination experiment, couldn't be completely emptied before

the beginning of decontamination, and the diffusion of pollutant from sand tank toward IT occurred, too. The initial conditions in the aquifer are variable like in Fig. 8 b (measured concentration for  $t=0$ ).

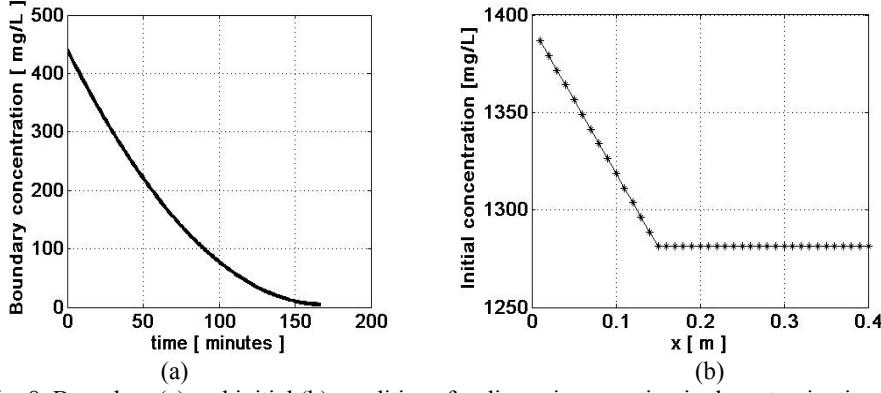


Fig. 8. Boundary (a) and initial (b) conditions for dispersion equation in decontamination case.

The numerical values of pollutant concentrations obtained for two retardation factors  $R=1$  (no retardation) and  $R=1.8$  (Fig. 9) are compared with the measured concentrations (Fig. 10). For  $R=1$ , decontamination occurs more rapidly than for  $R=1.8$  (Fig. 9).

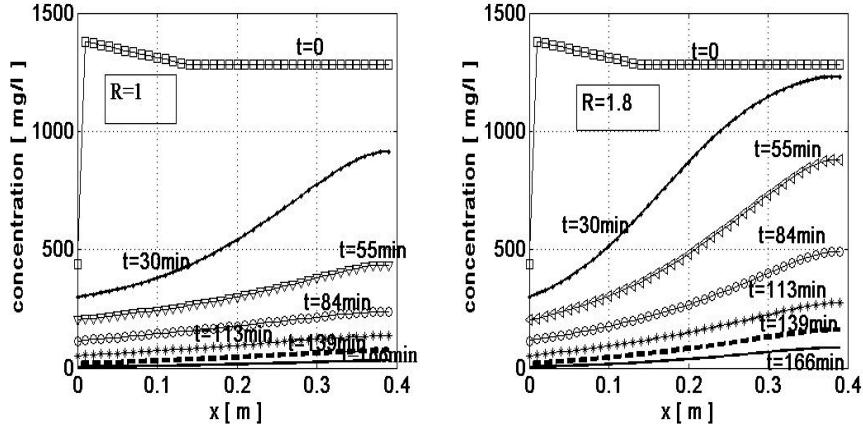


Fig. 9. Concentration  $C(x,t,R)$ , along the aquifer, at different moments,  $t$ , during contamination. a)  $R=1$ , b)  $R=1.8$ .

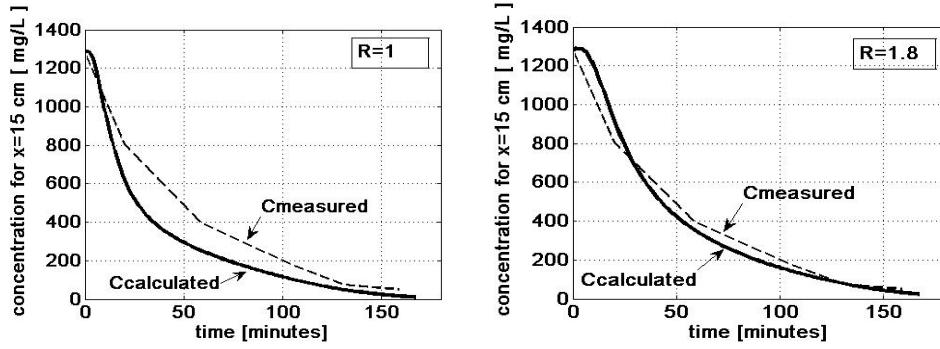


Fig.10. Time variation of concentration  $C(x,t)$ , at a distances  $x=15$  cm, for two values of retardation factor. Decontamination case.

## 5. Conclusions

We calibrated a simple, robust model to predict the pollutant concentration in an unconfined aquifer, using experimental data. Two experiments (pollution and decontamination) were performed providing data concerning the adsorption and desorption processes. The presented above results describes the retardation factor influence on the pollutant transport evolution. Using an optimization procedure, minimizing the differences between the numerical and experimental data, we calculated the retardation factor for potassium permanganate solute transport in our aquifer. For each extraction tube position ( $S_1-S_4$ ) decontamination efficiency (Fig.11 a) was calculated:

$$Decont. eff(x,t) = [(CI(x) - C(x,t))/CI(x)] \cdot 100 / WVU(t), \quad (21)$$

where  $WVU(t)$  is the total water volume used for decontamination until the moment “ $t$ ”, (Fig.11 b), and  $CI(x)$  is the initial pollutant concentration.

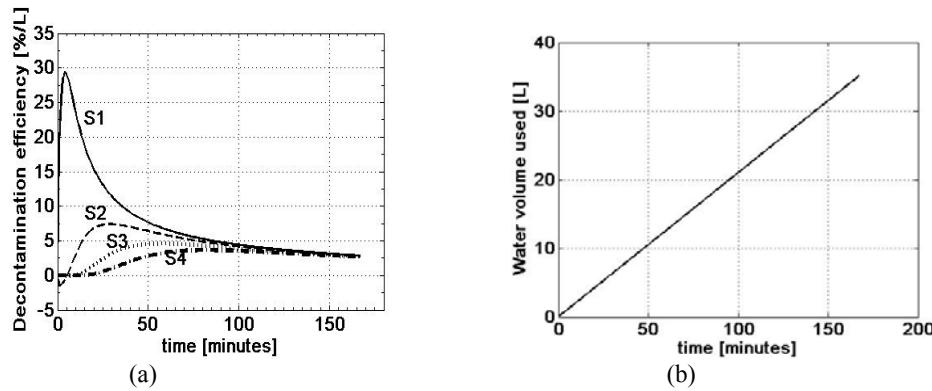


Fig.11.(a) Time variation of decontamination efficiency, at different distances along the aquifer.  
(b) Water volume used during the decontamination process.

The high efficiency values at the beginning of the process decrease in 50 minutes and after that an approximated constant value is maintained.

We intend to extend our research applying that model for decontamination of an aquifer polluted with nitrates.

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