

## TRANSPORT AND ADSORPTION OF POLLUTANTS IN SATURATED POROUS MEDIA: INTEGRATION INTO UNLIMITED DOMAIN

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### ABSTRACT

Adsorption and accumulation of persistent pollutants in soils, where the adsorption capacity of the soil itself is exhausted or unusual leaching or erosion events occur, may cause local groundwater degradation. In recent years, subsurface hydrological investigations, due to the increasing interest in site rehabilitation have shown a fast growth. Starting from the classical theories that preside over the phenomena of transport and transformation of pollutants in saturated porous media, the paper presents a direct integration approach of the transport equation over unlimited one-dimensional domains, valid for linear processes, which lead to many situations of practical interest. Lastly results are given as a function of three a-dimensional numbers.

**KEY WORDS :** Transport and adsorption, Groundwater pollutants, Direct integration method, Unlimited domain.

### INTRODUCTION

More than 90% of the world's current drinking water reserves come from groundwater, although its replenishable nature, in light of sustainability issue, we need to assume groundwater as a non-renewable resource, especially in areas where, due to various forms of pollution, the quality of these resources is compromised and restoration practices require time and resources.

The study of the motion processes of aqueous solutions in macroscopically homogeneous porous media, characterized by constant porosity, has been addressed by numerous authors (Kumar and Singh, 2015; Mousavi *et al.*, 2011; Remesikova, 2005; Neville *et al.*, 2000) referring to different and often recurrent situations in industrial and environmental applications such as the restoration phenomena of contaminated aquifers.

The development that numerical models are having in recent years and the existence of general numerical solutions for this type of problem is allowing a rapid growth in the interest of approaching this issue. These numerical solutions,

however, need to be verified, analytical and semi-analytical solutions can therefore act as a validation tool on the one hand and as a first approach tool to study such problems in the absence of experimental data. However, they have been developed and solved over the years for the study of transport and adsorption problems in homogeneous porous media and for simple or general form of time-dependent boundary conditions (Moranda *et al.*, 2018; Praveen Kumar *et al.*, 2014; Raji *et al.*, 2014; Kacur *et al.*, 2001).

Aim of this study is therefore to solve the classical one-dimensional pollutants transport-adsorption model on a non-conventional boundary condition, on one side to test the applicability of classical theories in these condition and on the other side to assess direct integration methodologies on a non-restrictive spatial discretization where standard finite difference and finite element solutions methods may generate uncertainty and numerical dispersion (Bobba *et al.*, 1995; Kinzelbach *et al.*, 1988).

An organic approach to the problem has been extensively treated in the bibliography (Russo

Spena and Todisco, 1990; Todisco *et al.*, 1994; Todisco 2008; Leu *et al.*, 1991) and will be referred to in the development of the present work.

### Theoretical background

Referring to the symbols shown in the appendix, considering a fixed control volume, in a system of orthogonal Cartesian coordinates, continuity equations written for both solute and solution respectively assumes the form:

$$\frac{\partial c\theta}{\partial t} = -\text{div}(c\theta\vec{v}) - \text{div}\vec{j} + Q \quad .. (1)$$

And

$$\frac{\partial \rho_m \theta}{\partial t} + \text{div}(\rho_m \theta \vec{v}) = 0 \quad .. (2)$$

Equation (2) became:

$$\rho_m \left[ \frac{\partial c_m}{\partial t} + \vec{v} + \text{grad} c_m \right] = -\text{div}\vec{j} + Q \quad .. (3)$$

Having considered:

$$c = \rho_m c_m \quad .. (4)$$

From eq.3 it follows that, in the absence of diffusion flow and production terms, the substantial derivative of  $c_m$  is zero, that is, the composition of each elementary volume of the solution remains stable during motion while the change in concentration of solute in the control volume is determined only by mechanical mixing.

The definition of the latter is closely linked to the determination of the field of vectors  $\vec{v}$ . The practical impossibility of obtaining a complete knowledge of this field induces to replace the actual movements of the solution, in the meatus of the porous media, with a global mean motion, determined by different forces derived from a scalar potential.

In the presence of very diluted solutions and in the absence of electric fields and significant chemical-physical phenomena, these potentials are related to the gravitational and pressure phenomena.

With these simplifications, considering the field occupied by the porous medium as if it were entirely occupied by the mixture, the Darcy relation is admitted:

$$\vec{v}_a = -k \text{grad} H_a \quad .. (5)$$

In which,  $\vec{v}_a$  and  $H_a$  represent, respectively, the solution's apparent velocity and the apparent piezometric load, both defined in all points of the space where the motion process takes place.

As regards the diffusive term of the solute in the

solution, it is essentially due, in isothermal terms, to the presence of concentration gradients, so that Fick's law is usually accepted:

$$\vec{j} = -D\theta \text{grad} \rho_m c_m \quad .. (6)$$

In the case of transport of polluting solute in porous systems, the diffusion coefficient  $D$  must necessarily consider not only the molecular diffusion  $D_m$  but also the mechanical dispersion of the  $D_k$  type. It is usually assumed, Fried, 1971:

$$D = D_m + D_k \quad .. (7)$$

Also, the phenomenon of adsorption is associated with the diffusive phenomenon when the contaminants have a relatively stable chemical structure. The latter does not remove the pollutant from the aqueous phase in a definitive way, but presides over many irreversible mechanisms of transformation and accumulation of the pollutant on the granules of the soil.

The correlation between adsorbed quantity per unit weight of the absorbent and solute concentration is expressed, at equilibrium, by the so-called adsorption isotherm:

$$S = k_s c^n \quad .. (8)$$

Where  $k_s$  is proportional to the surface available for adsorption and the constant  $n$  expresses the intensity of the adsorption itself.

Eq. (1) therefore, needs to be completed with a term that can take in account the accumulation of solute in the solid matrix. This term, considering adsorption isotherm (8), is expressed by:

$$\frac{\partial \rho S}{\partial t} = \rho k_s n c^{n-1} \frac{dc}{dt} \quad .. (9)$$

Where  $\rho$  is the apparent density of the porous media, and is assumed to be constant.

Presuming  $n=1$ , which corresponds to a wide range of common situations (Shahmohammadi-Kalalagh *et al.*, 2008; Dube *et al.*, 2001), equation (1) became:

$$\frac{\partial c}{\partial t} \left( 1 + \frac{\rho k_s}{\theta} \right) + v \frac{\partial c}{\partial z} = D \frac{\partial^2 c}{\partial x^2} + \frac{Q}{\theta} \quad .. (10)$$

The term  $(R = 1 + \rho k_s / \theta)$  is the so-called retard factor, it expresses the phase shift with which the front of the solute moves with respect to that of the solution. In the case of stationary solution motion, last equation specializes in:

$$\frac{\partial c}{\partial t} = D_0 \frac{\partial^2 c}{\partial x^2} - k_0 \frac{\partial c}{\partial x} - k_1 c \quad .. (11)$$

Where it is set  $D_0 = D/R$ ,  $k_0 = v/R$ , and  $k_1 = \zeta/\theta R$  having assumed for Q a first order reaction.

Eq. (11) was solved for a wide range of boundary conditions (Bischoff *et al.*, 1962; Brenner, 1985; Selim & Mansell, 1976). In particular, has shown by Russo Spena *et al.* (1990) for the resolution of the latter equation was developed a direct integration process for limited domains with generical initial condition and Neumann boundary conditions.

In this paper eq. 11 was solved referring to an unlimited domain, on one side making use of an appropriate device, which makes possible to bring the problem back to a function in the domain  $[0, \infty]$ , which assumes a fixed value at the boundary 0 (Dirichlet problem).

Calculation results where than reported as a nomogram, function of two a dimensional number that better characterizes the phenomenon.

**MATERIALS AND METHODS**

Let's consider a cylinder, indefinitely extended on one side, filled with granular material whose pores are uniformly saturated with water in uniform motion.

If the x axis is coincident with the pipe axis, at time  $t_0 = 0$  assumed as the origin of times, let's think to pump in, at  $x = 0$ , power supply section, a constant flux  $\varphi_0^*$  with concentration  $c_0$ .

When  $t > 0$ , the concentration c at the power supply section progressively increase and simultaneously a transport process is perfected in the  $x > 0$  direction governed by equation 8.

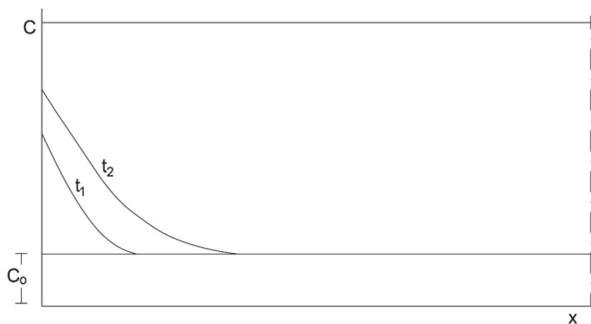


Fig. 1. Concentration profiles at t1 and t2

From fig. 1 one can assume the initial condition:  $c(x, 0) = c_0$

And condition at  $x \rightarrow \infty$  for  $\forall t > 0$

$c(\varphi, t) = c_0$

At  $x = 0$  is instead assigned the value of the flow of solution entered that, considering the positions previously made leads to the following:

$$\varphi_0 = k_0 c - D_0 \frac{\partial c}{\partial x} = k_0 c_0 \quad \dots (12)$$

Where  $\varphi_0$  is the ratio  $\varphi_0^*/R\theta$ , for the assumed condition  $\theta = c$ .

With this approach, the problem leads back to the search for the function  $c(x, t)$  such that, its derivative in the direction of the boundary normal  $x = 0$  is reduced to a function (in particular to a given constant (Neumann problem)).

A simple artifice therefore makes it possible to trace back the problem posed to the determination of a new function in the domain  $[0, \infty]$  which at the boundary  $x = 0$  assumes a predetermined value (Russo Spena and Todisco, 1990; Todisco *et al.*, 1994; Todisco, 2008).

In fact, deriving eq. 11 with respect to x we have:

$$\frac{\partial}{\partial t} \left( \frac{\partial c}{\partial x} \right) = D_0 \frac{\partial^2}{\partial x^2} \left( \frac{\partial c}{\partial x} \right) - k_0 \frac{\partial}{\partial x} \left( \frac{\partial c}{\partial x} \right) - k_1 \frac{\partial c}{\partial x}$$

this last equation, taking into account that:

$$\frac{\partial c}{\partial x} = \frac{k_0}{D_0} c - \frac{\varphi}{D_0} \quad \dots (12')$$

Holds out:

$$\frac{\partial \varphi}{\partial t} = D_0 \frac{\partial^2 \varphi}{\partial x^2} - k_0 \frac{\partial \varphi}{\partial x} - k_1 \varphi \quad \dots (13)$$

And initial and boundary conditions are:

$$\varphi(x, 0) = cost \quad \dots (14a)$$

$$\varphi(0, t) = \varphi_0 \quad \dots (14b)$$

$$\varphi(\infty, t) = 0 \quad \dots (14c)$$

To solve eq. 13 with 14a,b,c conditions we place:

$$\varphi(x, t) = \psi(x, t) \exp \left[ \frac{k_0 x}{2D_0} + \left( \frac{k_0^2}{4D_0} \right) t \right] \quad \dots (15)$$

Where  $\psi(x, t)$  is the unknown function to be determined.

Based on transformation (15), eq. (13) is reduced to the linear differential equation with constant parabolic coefficients:

$$\frac{\partial \psi}{\partial t} = D_0 \frac{\partial^2 \psi}{\partial x^2} \quad \dots (16)$$

Whereas, initial and boundary conditions (14a,b,c) find for  $\varphi(x, t)$  become:

$$\psi(x, 0) = cost \exp \left( -\frac{k_0 x}{2D_0} \right) = f(x) \quad \dots (17a)$$

$$\psi(0, t) = k_0 c_0 \exp \left[ \left( -k_1 - \frac{k_0^2}{4D_0} \right) t \right] = p(t) \quad \dots (17b)$$

$$\psi(\infty, t) = 0 \quad \dots (17c)$$

Highlighting (17b), one can see that  $\psi(0, t)$  at the extreme become a function of time even when the value of in (14b) is a constant.

The solution of equation (16), posing (17a,b,c), can be found breaking the unknown function into the sum of two other functions:

$$\psi(x, t) = \psi_1(x, t) + \psi_2(x, t) \quad \dots (18)$$

Where  $\psi_1(x, t)$  is solution of:

$$\frac{\partial \psi_1}{\partial t} = D_0 \frac{\partial^2 \psi_1}{\partial x^2} \quad \dots (19)$$

Subject to:

$$\psi_1(x, 0) = f(x) \quad \dots (20a)$$

$$\psi_1(0, t) = 0 \quad \dots (20b)$$

$$\psi_1(\infty, t) = 0 \quad \dots (20c)$$

Whereas  $\psi_2(x, 0)$  is solution of:

$$\frac{\partial \psi_2}{\partial t} = D_0 \frac{\partial^2 \psi_2}{\partial x^2} \quad \dots (21)$$

Subject to:

$$\psi_2(x, 0) = 0 \quad \dots (22a)$$

$$\psi_2(0, t) = p(t) \quad \dots (22b)$$

$$\psi_2(\infty, t) = 0 \quad \dots (22c)$$

Whereas  $\psi_2(x, t)$  is solution of:

$$\frac{\partial \psi_2}{\partial t} = D_0 \frac{\partial^2 \psi_2}{\partial x^2} \quad \dots (21)$$

Subject to:

$$\psi_2(x, 0) = 0 \quad \dots (22a)$$

$$\psi_2(0, t) = p(t) \quad \dots (22b)$$

$$\psi_2(\infty, t) = 0 \quad \dots (22c)$$

Equation (19) with the assigned initial and boundary conditions, admits the following particular integral:

$$\psi_1(x, t) = \frac{1}{2\sqrt{\pi D_0 t}} \int_0^\infty \left( e^{-\frac{(x-t)^2}{4D_0 t}} - e^{-\frac{(x+t)^2}{4D_0 t}} \right) f(\xi) d(\xi) \quad \dots 23$$

Solution of (20), when it is schematized  $p(t)$  with the stepped function (Marchi, 1961):

$$p(t) = \begin{cases} p_0 & t_0 < t < t_1 = t_0 + \Delta t \\ p_1 & t_1 < t < t_2 = t_1 + \Delta t \\ \vdots & \\ p_{n-1} & t_{n-1} < t \leq t_n = t_{n-1} + \Delta t \end{cases}$$

Where  $\Delta t = (t_n - t_0)/n$  is the width of the step,  $n$  is the number of parts in which the interval  $(t_n - t_0)$  is divided and it is indicate:

$$g(x, t - t_1) = \text{erfc} \left[ x / (2\sqrt{D_0(t - t_1)}) \right]$$

Is than furnished by:

$$\psi_2(x, t) = \sum_{i=0}^{n-2} p [g(x, t - t_i) - g(x, t - t_{i+1})] + p_{n-1} g(x, t_n - t_{n-1}) \quad \dots (24)$$

Given the position taken (18), it has ultimately:

$$\psi(x, t) = \frac{1}{2\sqrt{\pi D_0 t}} \int_0^\infty \left( e^{-\frac{(x-t)^2}{4D_0 t}} - e^{-\frac{(x+t)^2}{4D_0 t}} \right) f(\xi) d(\xi) + \sum_{i=0}^{n-2} p [g(x, t - t_i) - g(x, t - t_{i+1})] + p_{n-1} g(x, t_n - t_{n-1}) \quad \dots 25$$

This, based on equation (15), allow to calculate  $\varphi(x, t)$ , consequently, with respect to (12'), it goes up through integration to the  $c(x, t)$ :

$$c(x, t) = \frac{\exp(k_0 x / D_0)}{D_0} \int_x^\infty \exp(-k_0 \xi / D_0) \varphi(x, t) d\xi \quad \dots (26)$$

### RESULTS AND DISCUSSION

We solved equation (26), assuming certain values for the parameters  $D, \rho, \theta, k_s, v$ , as shown in Fig. 2, in this way it was possible to compare the results, plotting the variation in concentration over time, with the results obtained from Lindstrom *et al.*, 1967 using a different integration process.

From the comparison we note how, with the

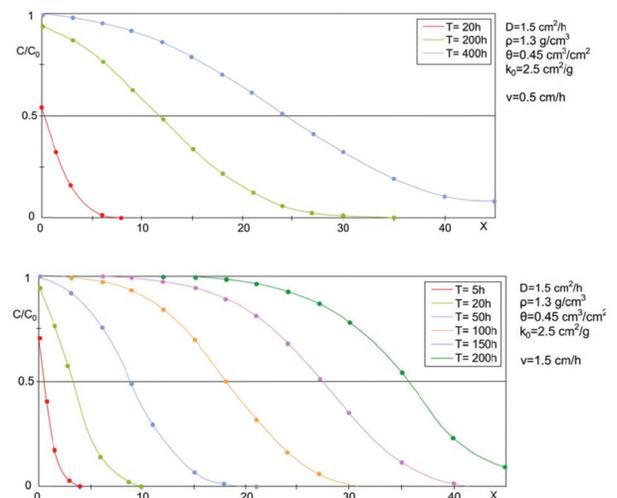


Fig. 2. Dynamic response of the column, that is the variation of the concentration along the column and over time. In panel (a) with the integration process here described, for  $t=20, 200, 400h$ ; In panel (b) as shown by Lindstrom *et al.* for  $t=5, 20, 80, 100, 150$  and  $200h$

same values, the concentration curves shape shows the same trend, differing in the amplitude of the transfer area of the matter.

The same solutions could be plotted in terms of three a-dimensional meaningful numbers, the diffusion ratio  $c/c_0$ , the time factor  $\tau = v_0^2 t/D$ , and the Peclet number  $Pe = k_0 x/D_0$ , i.e. the dimensionless number than can relate the effectiveness of mass transport by advection to the effectiveness of mass transport by either dispersion or diffusion (Huysmans *et al.*, 2005).

Thorough the deriving Nomogram, shown in Fig. 3, it is easy to obtain the concentration profiles related to various instants t, for situations congruent with the assumed hypotheses and for constant flow of the system.

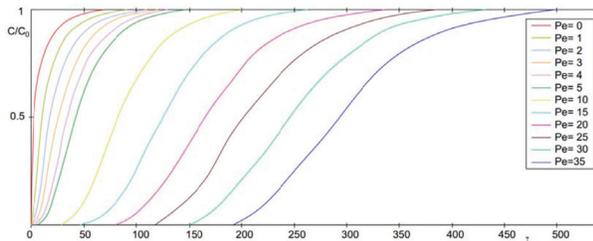


Fig. 3. Nomogram to determine the variation of solute at various distances from an extended front.

## CONCLUSION

In this paper we solved transport equation in saturated porous media (Eq. 26) addressing an integration process in which, through an appropriate artifice we were able to integrate those equation into unlimited domain. Results were compared to other solutions, given through a different integration process, shown similitudes, further corroborating that the methodology here described works well.

These analytical solutions can provide an acceptable indication of distribution of pollutants more quickly and cheaply than by monitoring network. Moreover, within assumed limitations, solutions would be also of practical interest for comparison with observations both in laboratory and on field.

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## Appendix

$c$  : Local concentration (mass of solute contained in

the unit of volume of the solution)

$c_m$  : Mass fraction (ratio between mass of solute and mass of solution, both referred to the unit of volume of the solution)

$\varepsilon$  : Porosity

$\theta$  : Volume of solution present in the volume unit of the porous medium

$\vec{v}$  : Actual speed of the solution at the instant t

$\vec{j}$  : Diffusion flow density (i.e. the mass of solute in transit in the unit of time through the area unit)

$\rho_m$  : Solution density

$Q$  : Production term, in the presence of chemical reactions

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