TRANSPORT OF REACTIVE POLLUTANTS IN GROUNDWATER. THEORETICAL AND NUMERICAL APPROACHES

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We study the transport of solutes in porous media considering the influence of chemical reactions.

The transport equation for advection dispersion can be extended to include the effects of retardation of solute transportation through sorption, chemical reaction, biological transformations, or radioactive decay and including source sink term.

The advance of the contaminant front is retarded as a result of the transfer by adsorption of the contaminant mass from the pore water to the solid part of the porous medium.

We will compare the numerical solution of the one dimensional advection – dispersion – adsorption equation with some analytical results, for the constant aquifer velocity case. We propose an implicit numerical approximation for the transport equation of reactive pollutants in an aquifer considering the variable water velocity. We have done a numerical analyze of the model sensitivity with respect to retardation factor, decay coefficient and production.

Keywords: groundwater, advection, dispersion, pollution, retardation factor.

1. Introduction

We analyze the transport of a pollutant traveling from a polluted lake or stream throughout an unconfined aquifer. The effects of retardation, sorption, chemical reaction, biological transformations, and radioactive decay are considered. The groundwater variable velocity is used in the dispersion-advection equation of the pollutant.

Our problem is to solve the advection-dispersion equation with retardation, sorption, chemical reaction, biological transformations, and radioactive decay for the unconfined aquifer, considering the variable velocity, and a mechanical dispersion in the porous medium [3]. For boundaries conditions we consider the polluted lake having a constant C_0 concentration, and at the outflow lake, an unknown concentration. The initial values of concentration in the aquifer are known.

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The influence of reactive pollutants transport is studied considering the difference between the advection-dispersion equation solutions for different retardation, decay and production factors. The variation of these differences, in time and space, shows when and where, the influence of retardation, decay and production is important.

2. Transport of reactive pollutants in porous media

Soil or groundwater is a disperse system often called an aqueous solution. In such solutions, pure water is the solvent (dispersant) and the dissolved constituents are the solutes (disperse phases). The disperse phase is classified according to particle size as molecular dissolved, colloidal dissolved or suspended substances.

Depending on the studied problem, migrants of interest in soil and groundwater may be real or colloidally dissolved or emulsified solid, liquid, or gaseous particles. Chemistry studies have shown that the elementary migrating particles dissolved in water are not free ions but complexes [2].

The most representative processes of water quality genesis in groundwater are: dissolution – precipitation reactions; complex formation and decay processes; acid – base reactions; oxidation – reduction reactions; microbial accumulation and degradation processes; adsorption – desorption reactions.

The "mobile/immobile" two–phase model assumes that all of the constituents in the subsurface can be assigned to either a mobile fluid m ixphase or the immobile rock matrix. In the groundwater zone, liquid water is usually the only mobile mixphase.

The transports of migrants in the subsurface water, proceeds by molecular diffusion, advection and hydrodynamic dispersion.

Convection (used synonymously with advection) is the transport of migrants due to bulk flow of a fluid mixphase in the subsurface, i.e., the mean statistical motion of all its components.

Hydrodynamic dispersion is the motion of subject migrants relative to the convective motion of the mixphase.

In a multiphase system subsurface [2], the convective transport of a migrant "i" in all fluid mixphases "j" is given by:

$$f\overrightarrow{C_{c,i}} = \sum_{j} \overrightarrow{q_j} C_{i,j} = \sum_{j} \sigma_j \overrightarrow{v_{a,j}} C_{i,j} \,, \tag{1}$$

where: $\overrightarrow{q_j}$ [LT^{-1}] is the Darcy velocity (volume flux density of the mixphase j);

$\overrightarrow{v_{a,j}}$ [LT^{-1}] is the average pore fluid velocity of the mixphase "j" ($v_{a,j} = \dfrac{v_j}{\sigma_j}$); σ_j

$[L^3 L^{-3}]$ is the volumetric content of the flowing fluid phase "j"; $C_{i,j}$ $[ML^{-3}]$ is the migrant "i" volumetric concentration in the fluid mixphases "j".

The Darcy velocity of the mixphase "j" is given by:

$$\overrightarrow{q_j} = -K_j \left(\frac{1}{\rho g} \, grad \, p + grad \, z \right), \tag{2}$$

where K_j $[LT^{-1}]$ is the hydraulic conductivity and p is the pressure in the fluid.

Most of considerations, simply superimposes molecular diffusion on hydrodynamic dispersion of the mobile phase and the resulting bulk transport of all constituents is:

$$f\overrightarrow{C_{Di}} = +\sum_j \left(- \sigma_j \, \overline{\overline{D}}_{D,i,j} \, grad \, C_{i,j} \right) \tag{3}$$

$\overline{\overline{D}}_{D,i,j}$ $[L^2 T^{-1}]$- is the hydrodynamic dispersion coefficient of migrant "i" in the mixphase "j", usually represented by a second order tensor.

Thus, the integral transport equation of migration processes in its common form is:

$$f\overrightarrow{C_i} = \sum_j \left(\overrightarrow{q_j} C_{i,j} - \sigma_j \overline{\overline{D}}_{D,i,j} \, grad \, C_{i,j} \right) \tag{4}$$

In the mixphase air, water and rock solids of the multiphase subsurface system, the migrants are subjected to numerous conversion processes.

Usually, the exchange processes are classified as filtering, sorption, ion exchange, dissolution and precipitation, external exchange processes (extraction of solute by roots and wells).

Sorption is the exchange 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 rock material, causing a decrease of solute concentration (causing a retardation of the contaminant transport). Desorption is the release of molecules and ions from the solid phase to the solute.

A sorption isotherm is the relationship between the solute concentration in the adsorbed phase and the concentration in the water phase.

For many contaminants that are of interest in groundwater studies the adsorption relationship can be expressed as:

$$S = K_d C^b \tag{5}$$

called Freundlich isotherm. S is the mass of solute species adsorbed or precipitated on the solids per unit bulk dry mass of the porous medium; C is the solute concentration; K_d and b are coefficients depending on the solute species, nature of the porous medium and on the other conditions of the system. For b=1, the adsorption relationship is a "linear isotherm":

$$S = K_d C. \tag{6}$$

K_d is referred to as the distribution coefficient and is a representation of the partitioning between liquid and solids only if the reactions that cause the partitioning are fast and reversible [2], [4].

3. Mathematical description of the total migration process

The integral mathematical process equation consists of a system of partial differential equations with one subsystem for each migrant. Each equation expresses a balance for a migrant in one of the mixphases of the REV. A solute balance equation has the following structure:

$$TR = S + EX + IR + ESS, \tag{7}$$

where TR - transport; S - storage; EX - exchange; IR - internal reactions; ESS - external sources/skins.

The form of the partial differential equation describing one – dimensional transport of a chemical constituent through soil is [1], [2]:

$$\frac{\partial}{\partial x}\left(\theta D \frac{\partial C}{\partial x} - qC\right) = \frac{\partial}{\partial t}(\theta C + \rho_b S) + \mu_w \theta C + \mu_s \rho_b S - \gamma_w \theta - \gamma_s \rho_b \tag{8}$$

where: C is the solution's volumetric concentration [ML^{-3}] (mass of solute per unit volume of fluid); S is the adsorbed concentration [MM^{-1}]; θ is the volumetric moisture content [L^{3}L^{-3}]; D is the dispersion coefficient [L^{2}T^{-1}]; q is the volumetric flux [LT^{-1}], (Darcy's velocity); ρ_b is the porous medium bulk density [ML^{-3}]; μ_w is the rate constant for first–order decay in the liquid [T^{-1}]; μ_s is the rate constant for first–order decay in the soil phase of the soil [T^{-1}]; γ_w is the rate constant for zero–order production in the liquid [ML^{-3}T^{-1}]; γ_s is the rate constant for zero–order production in the soil phase [T^{-1}].

For a linear isotherm adsorption relationship (6), the chemical transport equation (8) takes the form:

$$\frac{\partial}{\partial x}\left(\theta D \frac{\partial C}{\partial x} - qC\right) = \frac{\partial}{\partial t}\left(\theta C\left(1 + \frac{\rho_b K_d}{\theta}\right)\right) + \theta C\left(\mu_w + \frac{\mu_s \rho_b K_d}{\theta}\right) -$$
$$- \theta\left(\gamma_w + \frac{\gamma_s \rho_b}{\theta}\right) \tag{9}$$

If a retardation factor

$$R = 1 + \frac{\rho_b K_d}{\theta}, \tag{10}$$

two rate coefficient, given by

$$\mu = \mu_w + \frac{\mu_s \rho_b K_d}{\theta}, \tag{11}$$

$$\gamma = \gamma_w + \frac{\gamma_s \, \rho_b}{\theta} \,, \tag{12}$$

and the interstitial or pore – water velocity

$$v = \frac{q}{\theta}, \tag{13}$$

are defined, the equation (9) can be written:

$$\frac{\partial}{\partial x}\left(\theta D \frac{\partial C}{\partial x} - v \,\theta \, C\right) = \frac{\partial}{\partial t}\left(C \,\theta \, R\right) + \theta \, C \,\mu - \theta \,\gamma \tag{14}$$

The equation (14) is valid for unsaturated soil and for saturated one (aquifers). Usually for an aquifer the effective porosity n_e is used instead of θ ($\theta = n_e$).

For a homogenous aquifer, n_e is constant

$$n_e \, \frac{\partial}{\partial x}\left(D \frac{\partial C}{\partial x} - v \, C\right) = n_e \, \frac{\partial}{\partial t}\left(C \, R\right) + n_e \, C \,\mu - n_e \,\gamma, \tag{15}$$

and for a constant retardation factor R the transport equation will be:

$$\frac{\partial}{\partial x}\left(D \frac{\partial C}{\partial x} - v \, C\right) = R \frac{\partial C}{\partial t} + C \,\mu - \gamma. \tag{16}$$

Considering a dynamic dispersion regime,

$$D = D_0 + \alpha \, |v| \approx \alpha |v| \,, \tag{17}$$

$$v = \frac{q}{n_e}, \tag{18}$$

where α is the dynamic dispersivity, in x direction; v is the interstitial average linear groundwater velocity; D_0 is the molecular effective diffusion coefficient.

The retardation factor ranges from 1 to 10000 [4]. Due to adsorption, a reactive solute will travel at a slower rate than the groundwater flow. The coefficients μ (relation 11) and γ (relation 12) are different for each problem.

Equations (14) and (16) can be used to solve contamination environmental problems in soils (14) or in groundwater (16).

4. Numerical solution of the one-dimensional convective-dispersive solute transport equation

Numerous analytical solutions of the one–dimensional convective–dispersive solute transport equation with constant coefficients have been published. The most common of these solutions are presented in [1]. The solutions are directly dependent on the initial and boundaries conditions.

We propose a numerical solution for the transport equation (16) with variable coefficients (v and D).

An implicit approximation is used to solve the equation

$$R\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D(x)\frac{\partial C}{\partial x}\right) - \frac{\partial}{\partial x}(v(x)C) - C\mu + \gamma \tag{19}$$

with $D(x)$ and $v(x)$ given by (17) and (18).

Considering an unconfined aquifer with variable $v(x)$ [3] the effects of retardation, decay, and production are studied. The equation (16) is a particular case of (19) (when $D(x)=D$ and $v(x)=v$, are constants) and the numerical solution can be compared with the analytical one.

The numerical procedure is identical with the one presented in [3]. The difference consists in considering the decay, retardation and production effects.

5. Results and conclusions

The numerical solution of (16) is compared with analytical one [1], obtained for the same initial and boundaries conditions [3]. The results confirm the stability and the convergence of the numerical used scheme.

Our goal is to understand the retardation, decay or production influence on the advection-dispersion equation solution. Obviously the influence of this phenomenon (Fig.2, 4, 8) is important, but is useful to appreciate when and where, in the aquifer, that influence is greater.
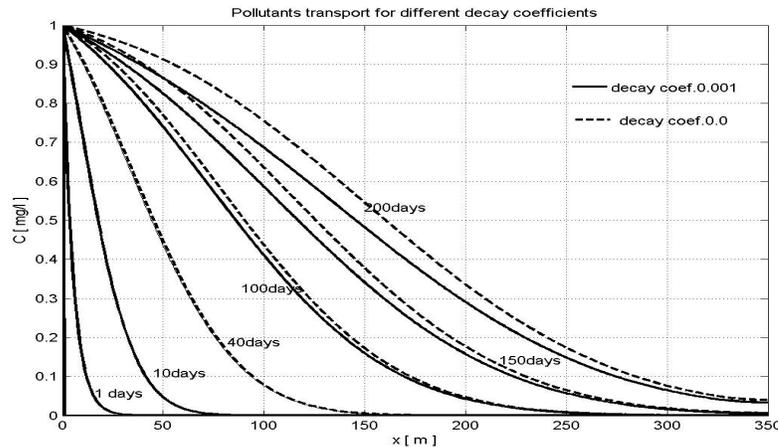
Fig. 1. Concentration for different decay coefficients ($\mu=0.001$ and $\mu=0$), for K=10m/day.

For each phenomenon, separately, will consider the solution of advection-dispersion equation without retardation, decay or production $C(x,t)$ and the solution obtained for a specific value of retardation factor R- (C_R), of decay coefficient, $\mu - (C_\mu)$, or of production coefficient, $\gamma - (C_\gamma)$.

We compare the results obtained for different decay coefficients (0.001, 0.01, 0.1, 1.0) with the solution obtained for μ=0. A relative, error is calculated:

$$\varepsilon_\mu\left(\%\right) = ((C - C_\mu)/C_0)\cdot 100,\qquad(20)$$

where C_μ is the matrix of $C(i, j)$, $(i = 1 : N, j = 1 : M)$ obtained for a variable velocity in the aquifer with a decay coefficient "μ", and C is the matrix of $C(i, j)$ for μ=0.

The lines corresponding to equals "$\varepsilon_\mu(x, t)$", in time end space can describe the importance of decay process in time, throughout the aquifer. (Fig.2)
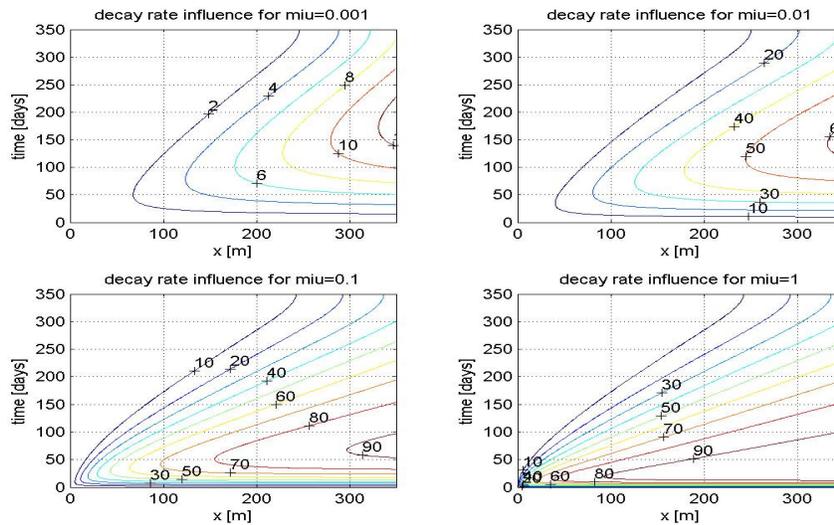
Fig. 2. Constant error "ε_μ (%)" contour for different decay coefficients (μ=0.001, 0.01;0.1;1), for K=10m/day.

The difference between the advection-dispersion solution neglecting decay term and the one obtained considering a decay coefficient, μ=0.001, is less then 10%. An error ε_μ >10% is obtained for μ=0.01 at x>40m, and for μ>0.1 at x>0. So for μ<0.001 the decay effect can be neglected, for K=10m/d.

We compare the results obtained for different retardation factors (2, 10, 100, 1000) of the pollutant in the aquifer with the solution obtained for R=1. A relative, error is calculated

$$\varepsilon_R\left(\%\right) = ((C - C_R)/C_0)\cdot 100,\qquad(21)$$

where C_R is the matrix of $C(i, j)$, $(i = 1 : N, j = 1 : M)$ obtained for a variable velocity in the aquifer with retardation factors R, and C is the matrix of $C(i, j)$ for R=1.

The lines corresponding to equals "$\varepsilon_R(x, t)$", can describe the importance of retardation process in time, throughout the aquifer. (Fig.4)
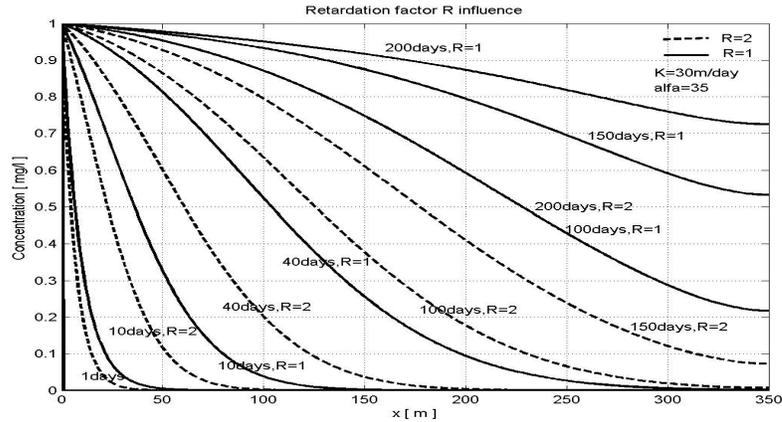
Fig. 3. Concentration for different retardation factors (R=2, R=1), for K=30m/day.
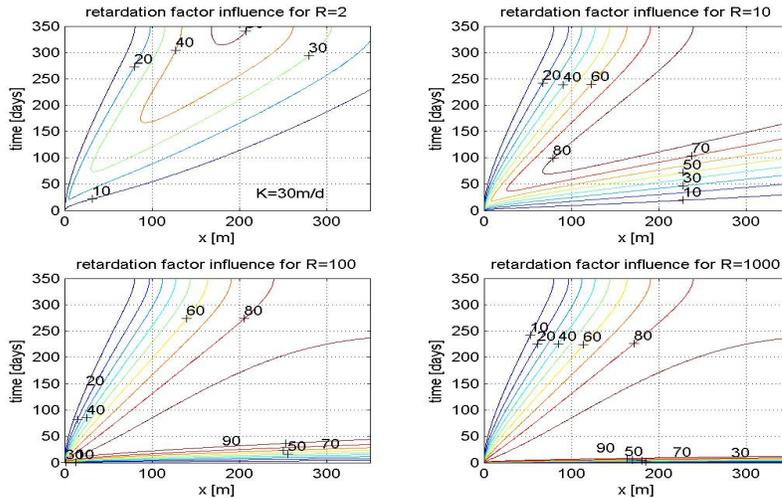
Fig. 4. Constant error "ε_R (%)" contour for different retardation factors (R=2; R=10; R=100; R=1000), for K=30m/day.

Considering a continuous pollution source concentration C0=1mg/l, in the space origin, x=0, a 0.5 mg/l concentration will be observed at the distance x=250m after 200 days for R=1, or after 100days for R=2 (Fig. 3).

For a less value of hydrodynamic conductivity, K, the retardation effect decreases.

A similar analyze, for production influence is done in Fig.5 and Fig.6.

$$\varepsilon_\gamma(\%) = ((C - C_\gamma)/C_0) \cdot 100 \qquad (22)$$
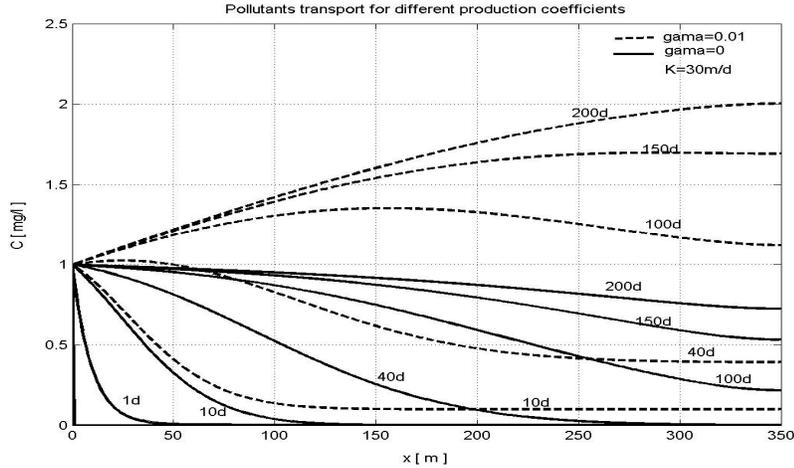
Fig. 5. Concentration for different production coefficients ($\gamma=0$, $\gamma=0.01$), for K=30m/day.

The influence of production coefficient is very important. For a $\gamma=0.001$, the influence of production can be neglected ($\varepsilon_\gamma<12\%$), but for $\gamma>0.001$, the $\varepsilon_\gamma>20\%$. The minus sign of errors indicates $C_\gamma>C$.
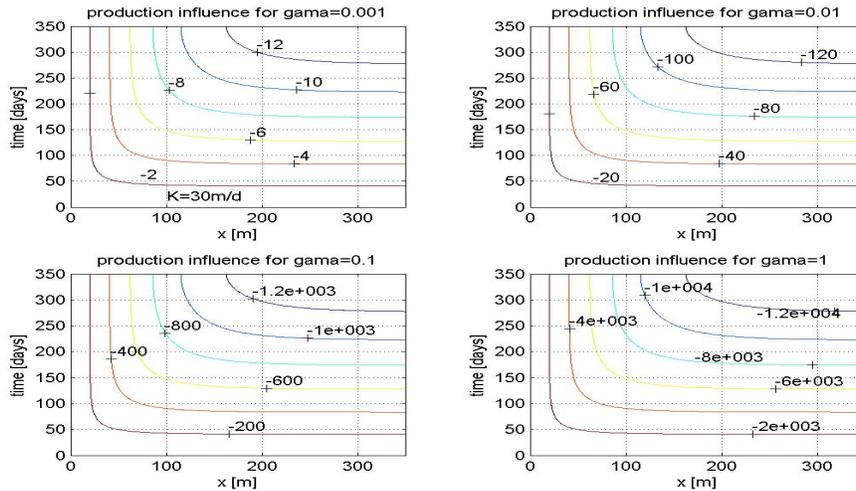
Fig. 6. Constant error "$\varepsilon_\gamma(\%)$" contour for different production coefficients ($\gamma=0.001$; $\gamma=0.01$; $\gamma=0.1$; $\gamma=1$), for K=30m/day.
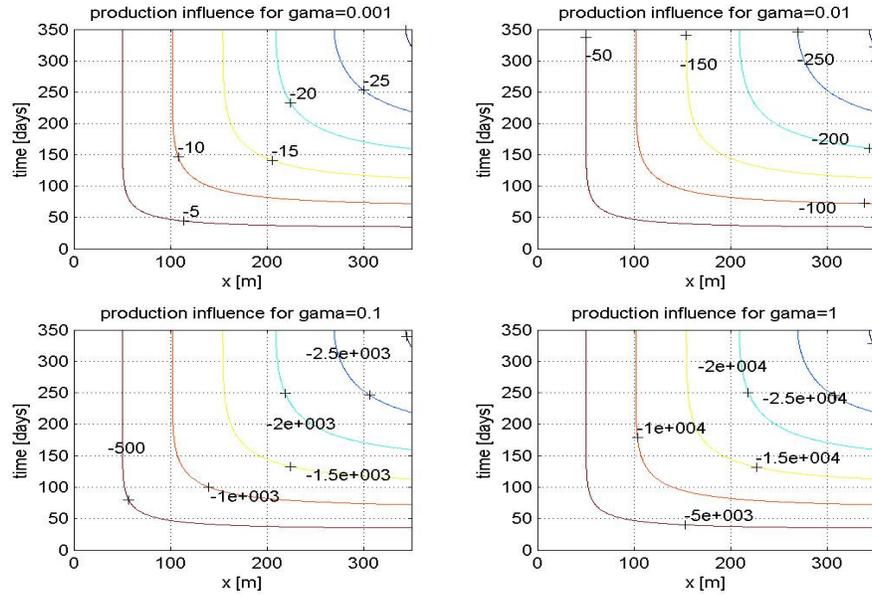
Fig. 7. Constant error "ε_γ (%)" contour for different production coefficients (γ=0.001; γ=0.01; γ=0.1; γ=1), for K=10m/day.

We compare the results obtained for different hydraulic conductivities, (K=30m/day - Fig.6, and K=10m/day –Fig.7). For a less value of K, ε_γ (%) increases, so always have to consider the effects of production.

The proposed numerical code is simple, robust, and can calculate the pollutant concentration considering retardation, decay and production, for an unconfined homogenous, isotropic, aquifer.

R E F E R E N C E S

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