

## THE ESTIMATION OF THE RADIONUCLIDE TRANSPORT PARAMETERS USING THE CDE MODEL

C. BUCUR<sup>1</sup>, M. OLTEANU<sup>1</sup>, M. PAVELESCU<sup>2</sup>

<sup>1</sup>*Institute for Nuclear Research, Pitesti, Romania; e-mail: crina.bucur@scn.ro*

<sup>2</sup>*Academy of Romanian Scientists – Bucharest, Romania*

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*Abstract.* Interest in contaminant transport has increased due to concerns about the fate of radionuclides in the subsurface environment, particularly with regard to the possible contamination of soil and groundwater by radioactive waste disposal both in near-surface and underground repositories. Although significant progress has been made, the quantitative description of contaminant transport in geological formations remains a challenging and active research area. This paper presents the estimation of transport parameters for a non-sorbing radionuclide (tritium) and a sorbing radionuclide (cesium-137) by fitting the experimental breakthrough curves with a Convection-Dispersion Equation (CDE) model. These experiments were performed in order to estimate the Barremian limestone dispersivity.

*Key words:* tritium, cesium, CDE model, breakthrough curve, limestone, transport parameters.

### INTRODUCTION

The Low and Intermediate Level (LIL) active waste generated by the Cernavoda Nuclear Power Plant will be disposed in a near-surface repository on Saligny site. Its close proximity to NPP, dry climate conditions, low water infiltration rates, and favorable geochemical properties exhibited by subsurface geologic horizons, are just a few of the characteristics that make Saligny site suitable for LIL radioactive waste disposal in Romania.

Geologically, the Saligny site structure consists of the sequence of the following geological units: silty loess (Horizon A), clayey loess (Horizon B), Quaternary red clay (Horizon C), Pre-Quaternary clay (Horizon D), Barremian limestone (Horizon E), Vallanginian clay, Jurassic limestone, Paleozoic sediments and the crystalline foundation of the green schist. The units significant for the long-term dose and risk assessment for the environment and population in the surrounding area are the fourth layers: horizon A, horizon B, horizon C, horizon D and horizon E. They contain the potential contamination pathways of the receptors [1].

Hydrologically, the site can be divided into a vadose zone down to 45–50 m and three distinct aquifers, two of them in the limestone beds (Eocene and

Barremian aquifers) and the third (Aptian aquifer) into the lenses of sand and limestone existing in the pre-Quaternary clay layer. The water table is around 11 m in elevation and changes according to the Danube level.

The LIL waste generated in a nuclear power plant contains a variety of radionuclides, but the vast majority of these radionuclides do not significantly contribute to potential human health impacts. Almost all of the disposed activity is found in relatively short-lived radionuclides, including  $^{137}\text{Cs}$ ,  $^{60}\text{Co}$ ,  $^{90}\text{Sr}$  and  $^3\text{H}$ .

The conceptual model for radionuclide release is aqueous, vapor, and gas phase migration from the waste form to the surrounding geological media. The cementitious waste form in combination with the trench liner will serve to greatly retard this migration. Aqueous phase transport will be controlled by the rate and quantity of infiltrating water and the radionuclides solubility. Infiltrating water will dissolve radionuclides and carry them in solution from the waste cell into the surrounding geological media. Vapor phase and gas phase radionuclides will diffuse from the waste; controlling parameters will include the radionuclides concentration and their diffusion coefficients.

Radionuclides of particular interest for this study are  $^{137}\text{Cs}$  and  $^3\text{H}$  (as tritiated water). Tritium was selected as nonreactive contaminant, while cesium is known as a very reactive contaminant especially in the geological formations with high clay content [2].

The *Barremian aquifer* is the main aquifer of the zone hosted by the limestone formation with the same name. It is situated underneath the loess and clays layers and is connected with the Danube River and Danube-Black Sea Canal, the Western and Southern site boundaries.

## CONTAMINANT TRANSPORT THEORY

It is useful to first consider the general character of contaminant transport experiments before presenting the experimental data fitting.

The convection–dispersion (also called as *advection–dispersion*) equation (CDE) is generally used to describe one-dimensional contaminant transport through a homogeneous medium during steady-state flow.

The CDE model of contaminant transport specifies that the total contaminant flux is:

$$J_s = J_w \cdot c_r - \theta \cdot D_d \cdot \frac{\partial c_r}{\partial x} - \theta \cdot D_m \cdot \frac{\partial c_r}{\partial x} \quad (1)$$

$$\left( \begin{array}{c} \text{convective} \\ \text{flux} \end{array} \right) \left( \begin{array}{c} \text{diffusive} \\ \text{flux} \end{array} \right) \left( \begin{array}{c} \text{dispersive} \\ \text{flux} \end{array} \right)$$

where:

$J_s$  – total contaminant flux density, [m/s];

- $J_w$  – volumetric water flux density (Darcy flux), [m/s];  
 $c_r$  – dissolved contaminant concentration – mass of dissolved contaminant per unit volume of soil water, [kg/m<sup>3</sup>];  
 $\theta$  – volumetric water content, [-];  
 $D_d$  – is the soil liquid diffusion coefficient, [m<sup>2</sup>/s];  
 $D_m(\theta, v)$  – mechanical dispersion coefficient, [m<sup>2</sup>/s].

The convection is defined as the passive movement of contaminant; diffusion is driven by concentration gradients according to Fick's law, while mechanical dispersion occurs because of local variability in the water velocity within and among pores [3]. Molecular diffusion can't be separated from mechanical dispersion in flowing groundwater and a single coefficient called the effective diffusion–dispersion coefficient (referred also to simply as the *dispersion coefficient*) is used:  $D = D_m + D_d$ .

$D_m$  depends on the pore structure, the contaminant velocity ( $v$ ), and the water content. The velocity dependence is expressed as:

$$D_m = \alpha \cdot v \quad (2)$$

where  $\alpha$  – is the dispersivity, [m].

Considering one-dimensional transport of a contaminant in a soil-water-air system and assuming that the solid phase is stationary and rigid, for a macroscopic volume of soil that contains no contaminant sink or sources the conservation mass requires:

$$\frac{\partial c_t}{\partial t} + \frac{\partial J_S}{\partial x} = 0 \quad (3)$$

where:

- $c_t$  – total contaminant concentration, [kg/m<sup>3</sup>];  
 $J_S$  – total contaminant flux density, [m/s];  
 $x$  and  $t$  are the space and time coordinates, [m and s, respectively].

Assuming a negligible amount of contaminant in the vapor phase, the total concentration is expressed as:

$$c_t = \rho_b \cdot S + \theta \cdot c_r \quad (4)$$

where:

- $\rho_b$  – soil bulk density, [kg/m<sup>3</sup>];  
 $S$  – sorbet contaminant concentration – mass of sorbed contaminant per mass of dry soil, [kg/m<sup>3</sup>].

With these considerations, the following form of CDE is obtained:

$$\frac{\partial(\rho_b \cdot S + \theta \cdot c_r)}{\partial t} = \frac{\partial}{\partial x} \left( \theta \cdot D \frac{\partial c_r}{\partial x} \right) - \frac{\partial(J_w c_r)}{\partial x} \quad (5)$$

The sorbed concentration is related to residual concentration through the sorption isotherm  $\Gamma$ , that defines the sorbed concentration at all times if sorption is instantaneous [4]:

$$S = \Gamma(c_r) \quad (6)$$

Although the sorption isotherm is nonlinear for most contaminants and soils, the linear isotherm may be a reasonable approximation at low contaminant concentration:

$$S = k_d c_r \quad (7)$$

where  $k_d$  is the contaminant distribution coefficient, [ $\text{m}^3/\text{kg}$ ].

The linear approximation is important because reduces Eq. (5) to a form that may be analytically solved. For steady water flow ( $\partial\theta/\partial t = 0$  and  $\partial J_w/\partial x = 0$ ) and uniform water content ( $\partial\theta/\partial x = 0$ ), Eq. (5) becomes:

$$R \frac{\partial c_r}{\partial t} = D \frac{\partial^2 c_r}{\partial x^2} - v \frac{\partial c_r}{\partial x} \quad (8)$$

where  $R$  is retardation factor, expressed for linear sorption as:

$$R = 1 + \frac{\rho_b \cdot k_d}{\theta} \quad (9)$$

Eq. (8) is the form of CDE most commonly used for estimating transport parameters from laboratory displacement experiments (column experiments).

In the case of a radioactive contaminant transport Eq. 8 has to be modified in order to account of degradation and production respectively:

$$R \frac{\partial c_r}{\partial t} = D \frac{\partial^2 c_r}{\partial x^2} - v \frac{\partial c_r}{\partial x} - \mu \cdot c_r + \gamma(x) \quad (10)$$

where:  $\mu$  and  $\gamma$  are combined first- and zero-order coefficients:

$$\mu = \mu_l + \frac{\rho_b \cdot k_d \cdot \mu_s}{\theta} \quad (11)$$

$$\gamma(x) = \gamma_l(x) + \frac{\rho_b \cdot \gamma_s(x)}{\theta} \quad (12)$$

where:

$\mu_l$  and  $\mu_s$  are first-order decay coefficients for contaminant degradation in liquid and adsorbed phases, respectively [ $\text{s}^{-1}$ ];

$\gamma_l$  is zero-order production terms for the liquid phase, [ $\text{s}^{-1}$ ];

$\gamma_s$  is zero-order production terms for the adsorbed phases, [ $\text{kg} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$ ].

It is sometimes useful to express Eq. (8) in terms of the dimensionless variable [5]:

$$R \frac{\partial C}{\partial T} = \frac{1}{P_e} \cdot \frac{\partial^2 C}{\partial X^2} - \frac{\partial C}{\partial X} - \mu^E \cdot C + \gamma^E(X) \quad (13)$$

where:

$T = vt/L$  – the number of pore volumes;

$X = x/L$  – characteristic length;

$P_e = vL/D$  – Peclet number;

$C = c/c_0$  – reduce volume average contaminant concentration;

$L$  – column length, [m];

$c_0$  – constant reference concentration, [kg/m<sup>3</sup>];

$v = J_w/\theta$  – average pore-water velocity, [m/s];

$\mu^E = \frac{L \cdot \mu}{v}$  – a first-order decay coefficient, [s<sup>-1</sup>];

$\gamma^E = \frac{L \cdot \gamma}{v \cdot c_0}$  – a zero-order production coefficient, [s<sup>-1</sup>].

Solutions for the CDE may be obtained for specified boundary and initial conditions. Proper formulation of boundary conditions for the analysis of column displacement experiments is critically important to the interpretation of observed data (usually expressed as effluent concentration versus time or pore volumes), as well as for subsequent extrapolation of the experimental results to transport problems in the field [6].

Experimentally measured breakthrough curves and depth profiles often exhibit asymmetries and tailing that are not consistent with the equilibrium CDE model (Eq. 13). Experiments have shown that the CDE provides a reasonably accurate description of nonreactive contaminant transport in uniformly packed, saturated laboratory columns. For reactive contaminants CDE predictions are often less satisfactory. A variety of mechanisms may cause transport to differ from CDE such as: nonlinear sorption isotherms, rate-limited sorption, immobile water and the presence of soil chemical and physical heterogeneities. For these situations, the nonequilibrium models have to be used to get the transport parameters from fitting the experimental breakthrough curves.

Nonequilibrium mechanisms can be classified as either physical or chemical. Physical nonequilibrium arises when macroscopic heterogeneities exist in the flow field (such as for structured soils – usually it is not the case of laboratory packed columns). Chemical nonequilibrium occurs when time-dependent sorption or exchange reactions are present.

The most used nonequilibrium models used to fit the experimentally breakthrough curves are:

- the two-region physical nonequilibrium model (TRM) – referred also to as the mobile-immobile model;
- the two-site model chemical nonequilibrium (TSM);
- the one-site model chemical nonequilibrium (OSM).

The *two region model* modifies the CDE model assuming that soil water is partitioned into mobile and immobile regions. Contaminant transport occurs by convection and diffusion-dispersion in the mobile water and it is transferred between the two regions by first-order diffusion process.

The *two site model* makes distinction between type-1 (equilibrium) sorption sites subject to instantaneous sorption and type-2 (first-order kinetic) sites where sorption obeys a kinetic rate law.

The two-site sorption model reduces to the *one-site fully kinetic sorption model* if only type-2 sites are presented.

Codes having implemented different type of transport models, both equilibrium and nonequilibrium, are available in order to use them to fit the experimentally breakthrough curves or concentration distribution.

## COLUMN EXPERIMENTS

Column experiments were performed on Saligny limestone cores in order to estimate the radionuclides transport parameters in Barremian limestone, the host rock of the main Saligny aquifer.

Experiments were run on four short columns; two of them contained 75–500 micron sieved crushed Saligny limestone while the other two were packed with crushed Saligny limestone having particle size distribution between 500 and 2000 microns.

The Barremian limestone platform consists in limestone rocks with different degrees of cracking and weathering in the upper part and in compact limestone in the lower part [7].

Experimentally values for transport parameters obtained for columns packed with finer limestone particles (75–500  $\mu\text{m}$ ) can approximate the transport parameters for intact healthy limestone while those gotten for coarser limestone particles (500–2000  $\mu\text{m}$ ) can characterize the transport parameters through the fractured, weathered limestone.

The bulk density was around 1414  $\text{kg}/\text{m}^3$  for columns packed with finer limestone particles and around 1285  $\text{kg}/\text{m}^3$  for columns with coarser limestone particles.

All columns had the characteristic length of around 46.16 cm and cross section of  $\sim 6.2 \text{ cm}^2$ .

Experiments were run under saturated conditions, columns being saturated using Saligny simulated water containing the main cations and anions found in the well water having an ionic strength of 26.5 mM and a pH of 8.47 [8].

Column experiments were conducted at two different injection rates: first run were performed at flow rate of 3 ml/hr and the second run at 0.75 ml/hr.

When steady-state water flow was established using Saligny simulated water, contaminant solution was injected (pulse input). For the first run, around 58 ml of contaminant solution containing 23275 CPM/ml of  $^3\text{H}$  and 10157 CPM/ml of  $^{137}\text{Cs}$  were injected for 19.5 hours. After contaminant solution was injected, the steady-state flow was kept injecting again the Saligny simulated water. The effluent solution was collected during almost 400 hours and samples were analyzed for tritium and cesium concentration (collection time interval was 2 hours).

Since the  $^{137}\text{Cs}$  wasn't detected in the effluents during the first experiments, in the second run 58 ml of solution containing only  $^3\text{H}$  (~ 22600 CPM/ml) were injected for 77 hours. Again in order to attain the steady-state flow, Saligny simulated water was injected before and after contaminant solution. Effluent solution was collected during 945 hours and measured for tritium and cesium concentration. For the second run, the time step for effluent collection was 7.5 hours. Neither during this second run experiment cesium was detected in the effluents.

The results from the experiments in columns 1 and 2 (finer particle size) were extremely similar, as well as those from the experiments in columns 3 and 4 (coarser particle size). For this reason only the results gotten by fitting the breakthrough curves from columns 1 and 3 will be presented in this paper.

## RESULTS AND DISCUSSION

Numerical values for transport parameters can be estimated by fitting the transport model to measured concentration distribution (expressed as  $C/C_0$  versus depth) or breakthrough curves (expressed usually as  $C/C_0$  versus time or as  $C/C_0$  versus the number of pore volumes). Parameters are estimated by adjusting the values until the concentration distribution predicted by the model agrees optimally with the measured data. The criterion used most often in transport parameters estimation is the last-squares criterion [9].

Tritium breakthrough curves were fitted using the STANDMODE program (Studio for Analytical Models for Solving the Convection-Dispersion Equation) in order to estimate its transport parameters. Two individual codes implemented in STANDMODE program were used for the breakthrough curves fitting: CXTFIT code developed for estimating transport parameters from laboratory and field tracer test experiment [10] and CFITM code developed for estimating equilibrium transport parameters from solute displacement experiments [11]. Tritium is considered a conservative tracer (it has no retardation on geological formations) and the equilibrium model can estimate with good accuracy its breakthrough curve.

The parameters that can be estimated using CXTFIT code are average pore water velocity and dispersion coefficient while CFITM code estimates the dimensionless parameters: Peclet number and pulse (the number of pore volumes for time equal with the pulse duration).

In order to have good fits for reasonable transport parameters an estimated value for average pore water velocity was determined for each cell using the following equation:

$$v = \frac{q}{\eta_e} \quad (14)$$

where:

$q$  is Darcy flux expressed as flow rate over the flow area ( $q = Q/A$ ), [m/s];

$\eta_e$  is the effective porosity (pore volume in which water can flow), [-].

Since the experiments were run under saturated conditions the pore space was filled with water and the porosity ( $\eta_e$ ) can be estimated as the volumetric water content ( $\theta$ ). Knowing the water mass in each cell (by weighting cells before and after saturation) and the bulk density, the volumetric water content was calculated using the following relation:

$$\theta = \frac{m_w}{m_l} \cdot \frac{\rho_b}{\rho_w} \quad (15)$$

where:  $m_w$  – mass of water, [g];

$m_l$  – limestone mass, [g];

$\rho_b$  – limestone bulk density, [g/cm<sup>3</sup>];

$\rho_w$  – water density, g/cm<sup>3</sup> [~1g/cm<sup>3</sup>].

Knowing the characteristic dimensions for each cell (length and cross section), the flow rate used for each run in each cell, and the water content in each cell, Darcy flux and average pore water velocity were estimated.

The columns characteristic parameters are presented in Table 1.

Both codes used for the breakthrough curves fitting gave similar results for the tritium transport parameters. The parameters estimated and their associated statistics are presented in Table 2 for the column 1 and in Table 3 for column 3.

As tritium is known as nonreactive contaminant, its retardation factor was fixed at 1.

Table 1

Characteristic flow data for columns 1 and 3

Parameter	Col1_run1	Col1_run2	Col3_run1	Col3_run2
$L$ [cm]	46.16		46.16	
$A$ [cm <sup>2</sup> ]	6.13		6.24	
$\rho_b$ [g/cm <sup>3</sup> ]	1.41		1.29	
$\theta$ [-]	0.53		0.55	
Flow rate, $Q$ [ml/hr]	3	0.75	3	0.75
Darcy flux, $q$ [cm/hr]	0.49	0.12	0.48	0.12
Pore water velocity, $v$ [cm/hr]	0.93	0.23	0.87	0.22



Table 2

Transport parameters obtained by tritium breakthrough curves fitting using CXTFIT for finer and coarser limestone particles (column 1 and column 3, respectively)

Param.	Value	S.E. coeff.	T-value	95% confidence limits	
				lower	upper
<b>col1_run1</b>					
<i>v</i> [cm/hr]	0.9984	1.543E-3	647.3	0.9954	1.002
<i>D</i> [cm <sup>2</sup> /hr]	0.5095	1.183E-2	43.07	0.4859	0.5331
<b>col1_run2</b>					
<i>v</i> [cm/hr]	0.2539	1.687E-4	1503	0.2533	0.2539
<i>D</i> [cm <sup>2</sup> /hr]	0.0985	1.209E-3	81.50	0.0961	0.1009
<b>col3_run1</b>					
<i>v</i> [cm/hr]	0.8733	5.961E-4	1465	0.8721	0.8745
<i>D</i> [cm <sup>2</sup> /hr]	0.0978	2.684E-3	36.44	0.0924	0.1032
<b>col3_run2</b>					
<i>v</i> [cm/hr]	0.2251	1.534E-4	1467	0.2248	0.2254
<i>D</i> [cm <sup>2</sup> /hr]	0.0404	8.389E-4	48.14	0.03874	0.04204

Table 3

Transport parameters calculated on the bases of those estimated by tritium breakthrough curves fitting

	column 1 (75–500 mm)		column 3 (500–2000 mm)	
	run1 (3 ml/hr)	run2 (0.75 ml/hr)	run1 (3 ml/hr)	run2 (0.75 ml/hr)
Peclet	90.45	118.99	412.18	257.19
Pulse	0.42	0.42	0.37	0.38
$\alpha$ [cm]	0.51	0.39	0.11	0.18

Tritium breakthrough curves for columns 1 and 3 are presented in Fig. 1 for the fast injection rate (3 mL/hr) and in Fig. 2 for the slow injection rate (0.75 mL/hr). Plots represent both the experimental breakthrough curves and the fitted ones using CXTFIT code. These plots show the very good reproducibility of the tritium breakthrough curves in each column, despite the fact that the flow rates were different in the two experiments in each column.

The dimensionless parameters that characterized the tritium transport in barremian limestone, at the laboratory scale, were calculated using the appropriate equation from parameters estimated by breakthrough curves fitting. These values are presented in Table 3.

Previous study on cesium sorption on loess and clay samples characteristic to the Saligny unsaturated zone have shown that this radionuclide is very strong sorbed on the Saligny geological formation [2]. Despite of this, cesium was introduced in the column study because of its high potential to be sorbed onto the

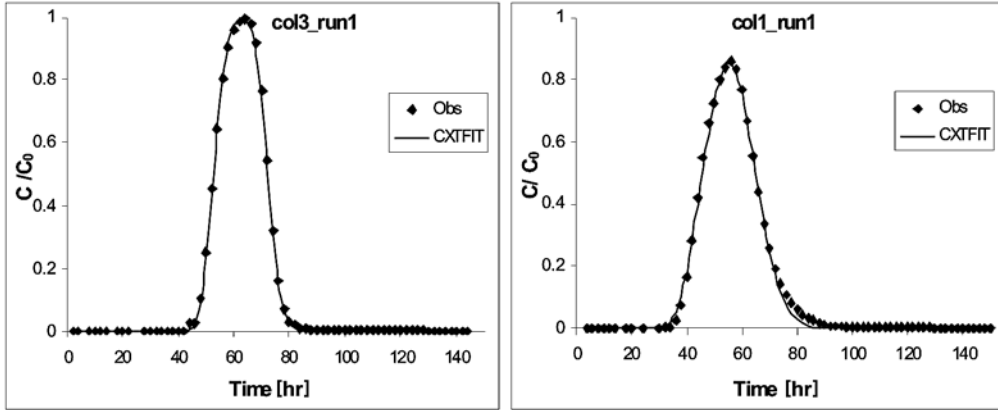


Fig. 1 – Tritium breakthrough curves for the first run (3ml/hr).

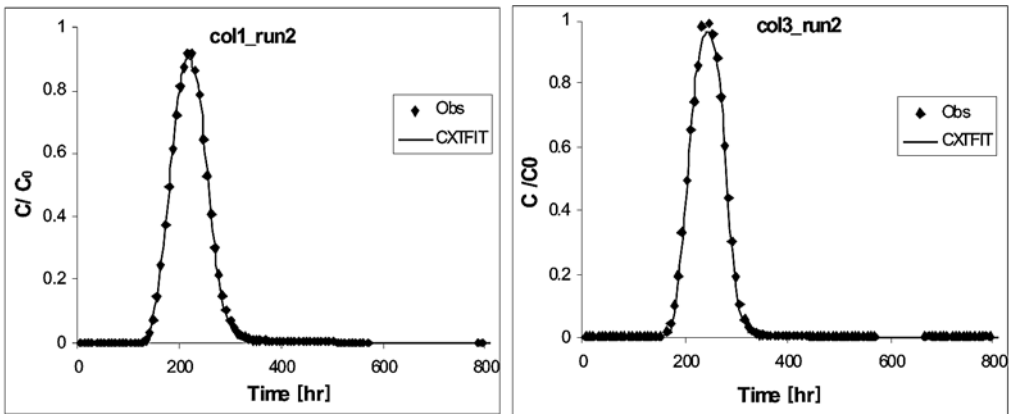


Fig. 2 – Tritium breakthrough curves for the second run (0.75 ml/hr).

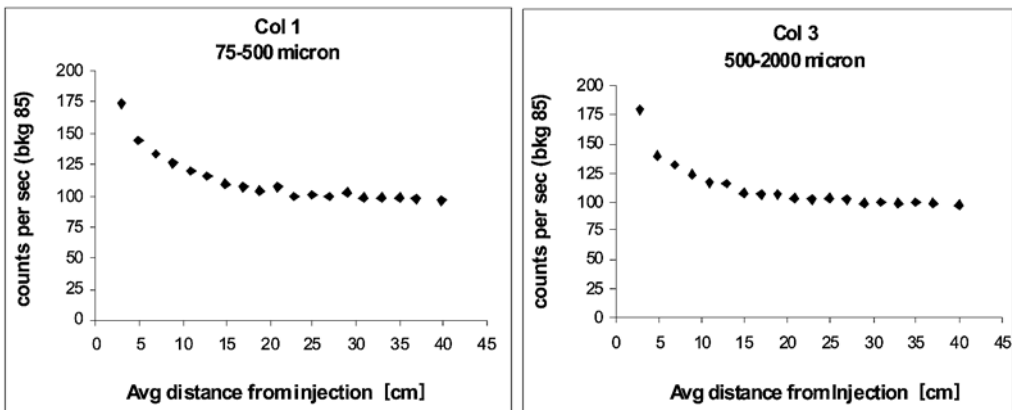


Fig. 3 – Cesium distribution in columns 1 and 3.

colloidal particles and to be transported through the vadose zone. Since during the two experiment runs cesium wasn't detected in the effluents a gamma probe was used to scan the columns in order to estimate the final distribution of Cs-137. Fig. 3 shows the qualitative results of gamma scans for columns 1 and 3.

## CONCLUSIONS

The limestone dispersivity was calculated based on tritium transport parameters. It is around 0.45 cm for the column packed with coarser limestone particles and around 0.15 cm for column packed with finer limestone particles. This means that in the first meters of the Barremian limestone platform, the contaminant plum is more dispersed in the longitudinal direction than in the deeper part of this rock. In the saturated zone, the water flows mainly in the horizontal direction and once released from the vadose in the Barremian aquifer, the non-sorbing contaminants and those that present low sorption on geosphere (such as  $^{14}\text{C}$ ) will be fast transported to the aquifer discharge points such as a well supplied by Barremian aquifer or the surface waters connected with this aquifer.

The experimentally results obtained for  $^{137}\text{Cs}$  show that even if this highly sorbing radionuclide crosses the vadose zone, it presents a very strong sorption on limestone. Consequently, this radionuclide will not reach the aquifer discharge points.

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