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Modeling of ^{137}Cs and ^{60}Co transport in calcareous soils by groundwater

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The fate of transport of radionuclides is one of the most important factors to be considered for the safety assessment of repositories of radioactive wastes in porous media. Laboratory batch and column experiments were investigated to assess the transport of ^{137}Cs and ^{60}Co in calcareous loam and clay soils leached with groundwater (GW) using convection-dispersion equation model (CDE). Fractionation of Cs and Co in eight sequential fractions in the soils was also measured. Results showed that the distribution coefficient (K_d) values for ^{137}Cs found to be much more as compared to ^{60}Co . It was ranged from 20 to 395 ml/g, depending on soil and radionuclide characteristics. The CDE model provided a fairly good fit to the experimental breakthrough curves (BTCs) of both solutes. The retardation factor (R) was 821 and 118 for ^{137}Cs , while it was 65 and 88 for ^{60}Co , for both soils, respectively. The dispersion coefficient (D) was 2.0 and 2.8 for Cs, and 0.6 and 0.7 cm^2/min for Co for loam and clay soils, respectively. The silt+clay was the major soil fraction in retaining Cs followed by sand fraction, for both soils, while the carbonate was the major soil fraction in retaining Co followed by silt+clay, Fe oxides, and sand for loam soil, and silt+clay, sand and Fe oxides for clay soil. No large change was observed in ^{137}Cs retaining with leaching. The leaching consistently reduced the magnitude of ^{60}Co bound to carbonate and increased fraction bound to silt+clay.

Key words: Transport parameters, ^{137}Cs , ^{60}Co , fractionation, dispersion, calcareous soils.

INTRODUCTION

The release of radioactive materials and fallout to soils has become important task with the advent of nuclear industry. Radionuclides reach groundwater (GW), plants and humans through several paths after their release to the environment. Therefore, the study of radionuclides transport through the soil is an important issue in the safety assessment of nuclear waste repositories and the potential for contamination. These materials can be immobilized in soil components by different mechanisms

such as adsorption. It has been recognized that the adsorption process to the soil matrix could limit the transport of radionuclides in the groundwater system (Haque et al., 2011). The mobility of radionuclides is associated with physiochemical characteristics of soil.

The presence of radionuclides like ^{137}Cs and ^{60}Co in the terrestrial environment may be conditioned by nuclear power reactors, nuclear weapon test and nuclear accident. They are part of the major contributors to the

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radionuclides inventory at low-level liquid waste disposal facilities (Serne et al., 1996). The interaction of radionuclide with the constituents of soil has been recognized as one of the most important processes determining the migration of radionuclide to groundwater. Migration of Co and Cs radionuclides in soil/groundwater system is important for safety disposal radioactive waste containing of these nuclides. Investigations on the behavior of radioactive Cs and Co in soil are addressed in many publications (Xiangke et al., 1999; Hakem et al., 2000; Shihab et al., 2001; Solovitch-Vella and Garnier, 2006; Itakura et al., 2010; Seliman et al., 2010, 2012). Those publications determined some factors affecting the movement of radiocesium or/and radiocobalt in soil.

Mathematical models are integral component of radionuclide transport in soil. An accurate understanding of this transport is required to successfully formulated and use these models. Palagyi and Stamberg (2010) found that the modified convection dispersion equation (CDE) gives rather better results for transport of ^{125}I , ^{137}Cs , and ^{85}Sr in granitoidic rock and soil columns than the classical one. Limited information on the Cs and Co transport parameters such as dispersion coefficient (D), retardation factor (R), and column Peclet number (P) as well as distribution of these radionuclides in soil exists in the literature.

The presence of carbonate in the soil may lead to increase its sorption capacity for radionuclides from radioactive waste and thus decreases their transport. Fahad et al. (1989) had indicated that soil carbonate is an important constituent in the retaining of applied ^{137}Cs . Although, the carbonate fraction of soil plays a key role in the sorption-desorption processes, the effect of carbonate on Cs and Co transport and distribution among soil constituents are still disputable.

The main objective of present study was to investigate the background or feature of calcareous soils in association with groundwater to fit the target radionuclide waste disposal. This was done by (1) evaluating the applicability of convection-dispersion equation model in describing transport of ^{137}Cs and ^{60}Co to understand the impact of leaching with groundwater on radioactive materials disposal under static and dynamic conditions, (2) estimate the transport parameters in undisturbed soil columns, and (3) determine the association of radionuclides with soil constituents using fractionation technique.

MATERIALS AND METHODS

The soils used in this study were calcareous and alluvial loam (soil 1) and clay (soil 2). These soils were taken from two locations surrounding the site of temporary storage of the low level radioactive liquid waste (LW), (formerly, Nuclear Research Center, Iraqi Atomic Energy Commission). Its location is within $33^{\circ}12'14''\text{N}$ $44^{\circ}30'49''\text{E}$. Some characteristics of the soils are given in Table 1, which determined by using standard procedure (Page et al., 1982; Klute, 1986).

Batch experiments

The distribution coefficient (K_d) (radionuclide sorbed on soil/radionuclide in solution) of ^{137}Cs and ^{60}Co were determined by the batch technique on samples taken from the surface soil (0-50 cm). The samples were mixed, air dried and ground to pass through a 2 mm sieve. One gram from each sample was equilibrated with the GW (EC= 6.5 dS/m, pH= 7.8 and containing of Ca=275, Mg=314, Na=1067, K=7.0, Cl=1525, SO_4 =887, and HCO_3 =177 mg/L), for 24 h in a 50 ml centrifuge tubes at 25°C . Borehole was drilled, penetrated the aquifer of the site, and used for obtaining samples of GW. The equilibrating solution was a carrier solution of specified radionuclides in 10:1 liquid to solid ratio. The concentration of nuclide in solution was 10^{-6} mol/L, prepared in GW taken from the aquifer of the same site, and labeled with 0.37 MBq (10 $\mu\text{Ci/ml}$) of CsCl and CoCl_2 . After equilibrium time, the mixture was then centrifuged for 15 h at 3500 rpm and a aliquot of 10 ml was pipetted from the supernatant solution. Activity of ^{137}Cs and ^{60}Co was measured in the 1 ml solution sample in 2 ml stoppered plastic vials, using a well-type NaI(Tl) detector (LKB,1282 Compugamma, Sweden). The instrument was programmed to count pulses corresponding to energy peak of 0.66 and 1.33 Mev for ^{137}Cs and ^{60}Co , respectively.

Preliminary experiments were used the two soils, two concentrations (10^{-10} and 10^{-6} mol/l), two ratios of liquid to solid (1:1 and 50:1), and four shaking times (2, 15, 24, and 48 h) to select the suitable shaking time. It was found that the sorption equilibrium was attained in 15 h for most cases (data not presented). For this reason a shaking of 15 h was adopted throughout the batch experiments. The amounts of radionuclide retained by sample were determined by subtracting the amounts of radionuclide remaining in the equilibrium solution from the amounts initially added. The K_d was calculated according to the following equation:

$$K_d = \frac{q}{c} = r \left(\frac{A_0}{r - A_1} \right) / A_1 \quad (1)$$

Where: K_d = distribution coefficient ($\text{L}^3 \text{M}^{-1}$), q = moles of radionuclide/g soil, c = moles of radionuclide/ml liquid, r = liquid to solid ratio, A_0 = total radionuclides applied (count rate), A_1 = radionuclide remaining in solution (count rate).

Column experiments

Undisturbed soil columns were sampled in Perspex tubes 0.5 m long and 0.05 m inner diameter. A steady state saturation water content condition in the soil columns was established before application of radionuclides (the soil columns were saturated with GW from the bottom). Each soil column was spiked with 1.48 MBq (40 μCi) for ^{137}Cs and ^{60}Co (carrier free). The soil columns then were leached with GW until ^{137}Cs and ^{60}Co until very small activity of ^{137}Cs and ^{60}Co was detected in the effluent. The GW was supplied through Mariotte technique maintaining a constant level of 2 cm throughout the leaching period, Table 2 presents physical parameters of soil columns. During the leaching process samples of effluent were daily collected by a fraction collector and measured for ^{137}Cs and ^{60}Co , using a well-type NaI(Tl) detector (LKB, 1282 Compugamma, Sweden) with aid of dual-label program. Data of ^{137}Cs and ^{60}Co from batch and column experiments were corrected for background, dead time, decay and the contribution of high energy ^{60}Co in the low energy ^{137}Cs (spill over). At the end of leaching, the soil columns were sectioned every 2 cm. Soil from each section was air dried, ground and passed through a 2.00 mm

Table 1. Some characteristics of soils.

Character	Soils	
	Soil 1	Soil 2
Textural class	loam	clay
Clay (g/kg)	256	393
Silt (g/kg)	463	303
Sand (g/kg)	281	304
ECe ^a (dS/m)	1.0	1.1
pH	7.9	7.8
Equiv.CaCO ₃ (g/kg)	324	325
OM ^b (g/kg)	14.0	11.4
CEC ^c (cmol ⁺ /kg)	13.0	23.4
Soluble ions (mg/L)		
Ca ²⁺	178	108
Mg ²⁺	31.3	31.0
Na ⁺	13.6	28.3
K ⁺	17.9	8.6
Cl ⁻	266	337
SO ₄ ²⁻	52.9	67.2
Clay minerals (%)		
Dominant 50-90	S(M) ^d	S(M), Ch
Major 20-50	Ch	HM, P
Minor 5-20	P, HM	I
Trace < 5	K, V	V, K

^aelectrical conductivity of soil pest extract, ^borganic matter, ^ccation exchange capacity, ^d S=Smectite; M=Montmorillonite; Ch=Chlorite; P= Palygorskite; HM= Hydrous Mica; I=Illite; K=Kaolinite; V=Vermiculite.

Table 2. Physical parameters of soil columns for ¹³⁷Cs and ⁶⁰Co.

Parameter	¹³⁷ Cs		⁶⁰ Co	
	Soil 1	Soil 2	Soil 1	Soil 2
Soil column length, L (m)	0.5	0.5	0.5	0.5
Bulk density, ρ (Mg/m ³)	1.44	1.36	1.44	1.36
Porosity (%)	45.7	48.6	45.6	48.7
Sat.vol.water content, θ (cm ³ /cm ³)	0.452	0.481	0.450	0.482
Pore volume, V (cm ³)	443.0	471.4	441.0	472.4
Pore water velocity, v (cm/min)	0.023	0.027	0.022	0.028

sieve. Two grams from each section were taken to measure the activity of ¹³⁷Cs and ⁶⁰Co in the same plastic vials in the case of effluent.

Fractionation experiments

The upper 2 cm layer from each soil column was mixed thoroughly for fractionation of the remained unleached ¹³⁷Cs and ⁶⁰Co (major part of the two radionuclides had been accumulated in the upper 2

cm soil layer). Ten grams were taken and separated into the following 8 sequential fractions, water soluble, exchangeable, associated with carbonate, organic matter, Mn oxides, Fe oxides, sand, and silt+clay. The first seven fractions except for carbonate were taken following Shuman (1985). The carbonate and silt+clay fractions were taken following the procedure described by Fahad (1988). The carbonate fraction was obtained by washing the sample extracted for exchangeable form with 40 ml deionized water for 3 min and 150 ml 1.0 M NaOAc of pH 5 was added. The soil sample was shaken for 24 h centrifuged at 6000 rpm, and

measured for Cs and Co. The silt+clay fraction was separated by sedimentation. The residual sample (sand + silt + clay) was treated with 10 ml of 5% sodium hexametaphosphate and 140 ml of deionized water, shaken for 24 h and sieved through 50 μm sieve to separate sand from silt+clay. The silt+clay suspension was then transferred to 1.0 L cylinder and filled to mark. Based on Stocks' law of particle sedimentation in fluids, sample of 25 ml was pipetted at depth of 10 cm at time zero for silt+clay. The same procedure of fractionation was repeated on soil samples received same activity of ^{137}Cs and ^{60}Co and incubated for the same time of leaching near saturation water content at $25\pm 1^\circ\text{C}$. All results reported for batch, column and fractionation experiments are average of triplicate determinations expressed on a moisture free basis.

Theory of transport

The basic transport equation is called convection dispersion equation (CDE) (Skagges and Leij, 2002).

$$R \left(\frac{\partial c}{\partial t} \right) = D \left(\frac{\partial^2 c}{\partial x^2} \right) - v \left(\frac{\partial c}{\partial x} \right) \quad (2)$$

Where R is the retardation factor, c is the volume averaged solute concentration, t is time, x is distance, and v is water velocity, approximated by ratio q/θ , where q is the volumetric flux density and θ is volumetric water content. Equation 2 can be solved analytically for initial boundary conditions:

$$c(0, t) = c_0 \text{ and } \frac{\partial c}{\partial x}(x, t) = 0 \quad (3)$$

By assuming that solute distribution inside the column is not affected by an outflow boundary or effluent collection system, and considering the column to be part of an effectively semi-infinite system. Also, by assuming that the concentration is continuous at $x=L$ (length of soil column ($0 \leq x \leq L$)), the following equation can be used for solute transport in soil column in one direction for the relative concentration of effluent (c/c_0) in terms of pore volumes, V leached through the column and column Peclet number, P (van Genuchten and Wierenga, 1986):

$$\frac{c}{c_0} = \frac{1}{2} \operatorname{erfc} \left[\left(\frac{P}{2\sqrt{R-1}} \right)^{\frac{1}{2}} (R-1) \right] + \frac{1}{2} \exp(P) \operatorname{erfc} \left[\left(\frac{P}{2\sqrt{R-1}} \right)^{\frac{1}{2}} (R+1) \right] \quad (4)$$

$$\text{and } P = vL/D \quad (5)$$

where c/c_0 is the relative concentration and $\operatorname{erfc}(x)$ is the complementary error function ($1 - \operatorname{erf}(x)$). In general D depends on pore structure, the solute velocity, and water content. The velocity dependence is often as:

$$D = \lambda v \quad (6)$$

Where λ is the dispersivity (units of length).

Parameters determination

Experimental retardation factor (R_{exp})

R_{exp} was calculated, by using K_d values (determined from batch

experiments Equation 1), from the following equation:

$$R_{\text{exp}} = 1 + \left(\frac{\rho K_d}{\theta} \right) \quad (7)$$

where ρ is bulk density of soil column. The conditions for batch experiments were similar as possible to those of the column experiments.

Peclet number and dispersion coefficient

Breakthrough curves (BTCs) of ^{137}Cs and ^{60}Co were constructed in which the relative concentration (c/c_0) was plotted as a function of GW pore volumes (V), one pore volume equals to liquid capacity of soil column (Table 2), passed through soil columns. Estimation for P and hence for D can be obtained by matching a series of theoretical curves calculated from Equation (4) with the experimental one. If a reasonably good agreement is achieved (higher correlation coefficient, r and root mean square error (RMSE) the curve is the best fit and parameter is based on that curve (trial and error). Then D was calculated from Equation (5). Data were analyzed by Mathcad software.

RESULTS AND DISCUSSION

Figures 1 and 2 presented observed and predicted BTCs as a function of pore volumes of ^{137}Cs and ^{60}Co of the two soils, respectively. There was good agreement between experimental and theoretical curves (best fit) with significant correlation coefficient (r) greater than 0.9 in all cases studied, and the RMSE was ranged from 0.035 to 0.058. Such fairly well fit indicates the suitability of Equation (4) and (5) to evaluate the respective BTCs of ^{137}Cs and ^{60}Co and hence to estimate and determine the relative transport parameters (Table 3). However, there was some scatter in the theoretical BTCs in terms of shape and position for both solutes reflect the influence of soil characteristics, pore structure, and ion type.

The theoretical non symmetrical sigmoid shape BTCs according to Equation (4) has shown that P number has a substantial influence on both position and value of c/c_0 is seen in Figure 3. By increasing the P from 1 to 20 at constant R value ($R=100$), the curve position is shifted to the left. The position of BTCs depends on both P and R values and the BTCs shape, and the R value depends mainly on the P value (Palagyi and Vodickova, 2009). Also, from Figures 1 and 2 it can be seen that the investigated radionuclides are readily retained, and retention depends on type of soil and their chemical properties. The values of retention at the end of leaching were about 17, 25, 6, and 14% for ^{137}Cs and ^{60}Co of soil 1 and 2, respectively. The highest retention for ^{137}Cs and in less degree for ^{60}Co resulted in high values of K_d and R .

It seems that R values of ^{137}Cs are much higher than those for ^{60}Co (Table 3). Values of R were 821 and 118 observed for Cs and 65 and 88 for Co, indicates that

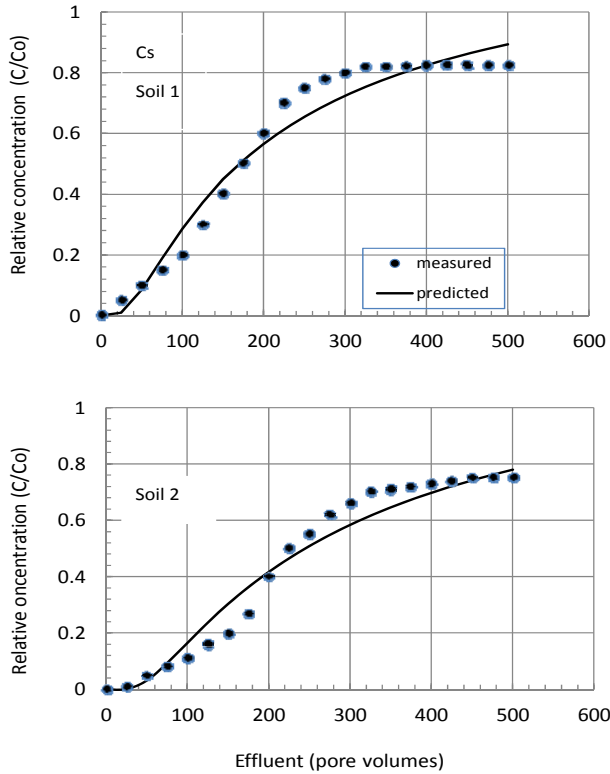


Figure 1. Experimental and theoretical breakthrough curves of ¹³⁷Cs retained on loam (soil 1) and clay (soil 2).

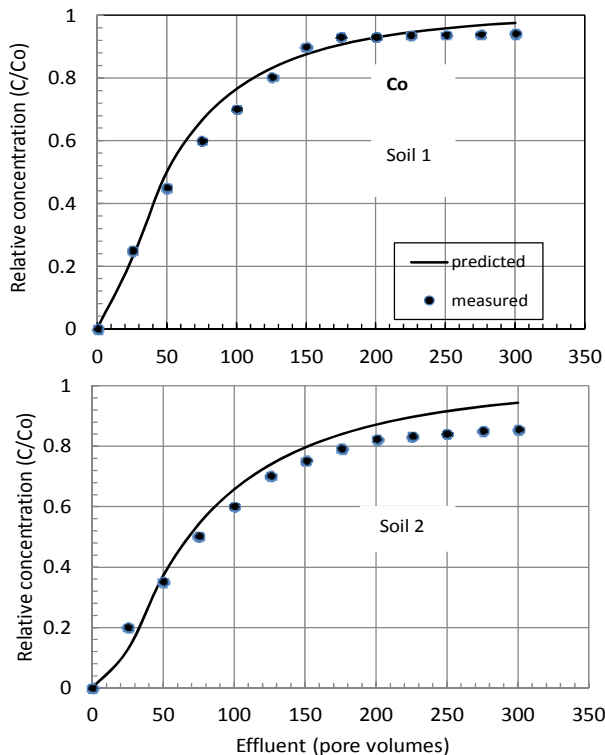


Figure 2. Experimental and theoretical breakthrough curves of ⁶⁰Co retained on loam (soil 1) and lay (soil 2).

¹³⁷Cs had been highly retarded comparison with ⁶⁰Co. Although nearly 500 and 300 pore volumes passed through the soil columns the amounts of Cs and Co retained were very high as indicated by the high retardation factors (*R*). The values of *R* calculated by using data obtained from batch-isotherm experiments were very representative of the observed transport of ¹³⁷Cs and ⁶⁰Co in the soil columns experiments. There is close correlation between experimental and theoretical *R* values, which only slightly differ from each other (*R*_{theo.} was obtained by BTCs fitting as above mentioned). The retention of these radionuclides, in accordance with the values of *K_d* is increasing in the order of ¹³⁷Cs > ⁶⁰Co. The *K_d* values were 257, and 395 for ¹³⁷Cs and 20, and 31 ml/g for ⁶⁰Co for soils 1 and 2, respectively (Table 3). It is clear that the *K_d* of ¹³⁷Cs is about 13 order of magnitude greater than for ⁶⁰Co in two soils.

The height values of *R* and *K_d* for Cs compared with Co had been obtained for two soils. The silt+clay content play large effect in retention process (Table 4). Clay content and type of clay minerals can play the role of natural barrier in the radionuclides migration (Bucur et al., 2000). Clay and silt have specific sites in their structures that strongly fixed the Cs ions. Cesium has low hydration energy, and if present at the site, it will lose the hydration shell and bind to the negatively charged mineral platelets, resulting in a closing of the site thus fixation the ion (Cornell, 1983). On the contrary, Palagyi et al. (2013) reported that ¹³⁷Cs sorption is irreversible despite of the fact that ¹³⁷Cs is prone to ion exchange and practically it forms no complexes.

It is obvious that ⁶⁰Co showed greater mobility than ¹³⁷Cs (Figures 1 and 2, Table 3). The ⁶⁰Co has relatively low sorption affinity to clay fraction. Based on series of studies Co was categorized as mobile, exchangeable, or irreversible sorbed in the sand sediment and water system (Mahara and Kudo, 1981). Also, mobile of ⁶⁰Co was found to consist of non ionic forms which do not contribute to ion exchange absorption onto soil matrix (Hossain et al., 2012). It is well known that cobalt hydrolyzes and form an insoluble hydroxide Co(OH)₂ in an alkaline solution. Therefore, under the conditions of the present study the migration rate of ⁶⁰Co in the soil columns faster than ¹³⁷Cs.

Radionuclides leached with GW were transported through the soil columns with mechanisms of diffusion. It moved in direction of the higher concentration to lower concentration (Bucur et al., 2006). Dispersion in soil was mainly affected by the geometry of porous structure and by the radionuclide interaction with pore walls (Haque et al., 2011). The relation between *D* and *P* (Equation (5)) is another important factor for recognizing the effect of both diffusion and dispersion on solute mixing. Although, the effects of both diffusion and dispersion on solute mixing are difficult to be separated, Fried and Combarnous (1971) suggested that when *P* is more than 20, the diffusion is at minimum value. Data in Table 3 show that *P* ranged from 0.5 to 2.0. This indicates that diffusion

Table 3. Transport parameters of ¹³⁷Cs and ⁶⁰Co in undisturbed soil columns.

Parameter	¹³⁷ Cs		⁶⁰ Co	
	Soil 1	Soil 2	Soil 1	Soil 2
K_d (ml/g)	257.5	394.9	20.2	31.1
R_{exp}	821.4	1117.6	64.4	87.7
R_{theo}	770	1200	65	88
P	0.5	0.5	2.0	2.0
D (cm ² /min)	2.1	2.8	0.6	0.7
λ (cm)	0.01	0.009	0.037	0.039
Correlation coeff., r	0.983	0.985	0.995	0.995
RMSE	0.056	0.053	0.035	0.058

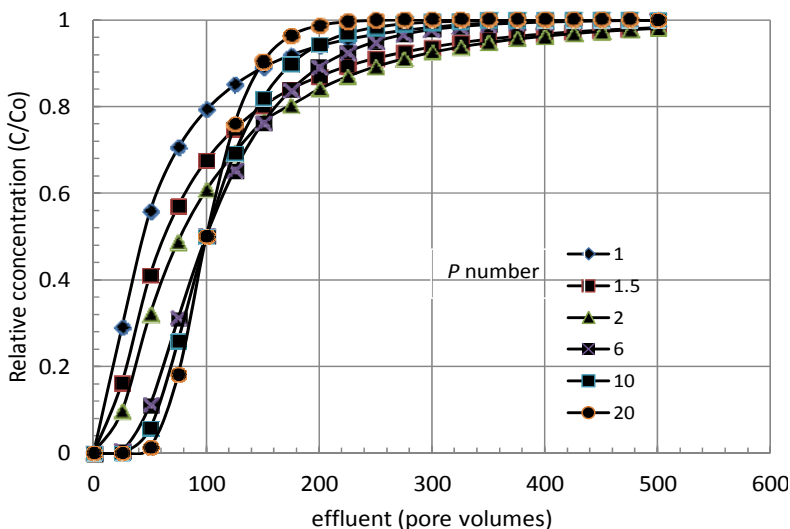


Figure 3. Effect of different values of P number on the position and shape of breakthrough curves at value of $R=100$.

may be the dominant process in transport of ¹³⁷Cs and ⁶⁰Co. On the other hand, D reaches values 2.1 and 2.8 cm²/min for ¹³⁷Cs and 0.6 and 0.7 cm²/min for ⁶⁰Co for the loam and clay soils, respectively. Also, λ values were 0.01 and 0.01 cm for ¹³⁷Cs and 0.04 and 0.04 cm for ⁶⁰Co for the loam and clay soils, respectively (Table 3). Regardless soil type, the highest value of λ being for ⁶⁰Co and the lowest for ¹³⁷Cs. It is evident that the reduction in λ values attributed to high reduction in flow velocities (Table 2).

In the present study the clay content of soils 1 and 2 were 256 and 392 g/kg, respectively (Table 1). Increasing CEC will therefore increase the exchange sites. Comparison of both soils showed that soil 2 had higher CEC, whereas soil 1 had lower CEC. Since clay fraction has a high affinity for sorption of Cs and Co, soil 2 sorbed

these two radionuclides higher than soil 1 (Figures 1 and 2). These results are in agreement with the reports of soil samples that contain clay minerals and resulted in large CEC for absorbing a large amount of dissolved ¹³⁷Cs (Kamel, 2010). When organic matter is higher, and clay minerals are not sufficient, the migration of radionuclide is higher (Dumat and Staunton, 1999; Rosen et al., 2006). This was not so in the present study, because the both soils have low organic matter (Table 1), therefore, the clay fraction plays large role in Cs and Co retention. Effect of length of soil column on travel time (t_r) of ¹³⁷Cs and ⁶⁰Co are shown in Figure 4. The travel time under dynamic conditions was calculated according to the following equation:

$$t_r = \left\lfloor \frac{L}{(v/R)} \right\rfloor \tag{8}$$

Table 4. Fractionation of Cs and Co remained in the upper layer 2 cm of soil column at the end of leaching.

Soil fraction	% of total added			
	¹³⁷ Cs		⁶⁰ Co	
	Control	Leached soil columns	Control	Leached soil columns
Soil 1				
Water soluble	0.3	0.3	0.3	2.3
Exchangeable	0.9	0.5	1.7	1.4
Carbonate	1.6	1.5	32.3	12.9
Organic	1.3	2.5	0.5	0.3
Mn oxides	1.0	0.9	4.5	3.0
Fe oxides	4.6	4.3	28.5	34.8
Sand	15.8	14.1	6.1	4.4
Silt+clay	74.5	75.5	26.5	41.0
Soil 2				
Water soluble	0.2	0.3	0.4	3.7
Exchangeable	1.1	0.4	2.5	2.1
Carbonate	1.9	1.4	47.3	23.7
Organic	1.3	4.4	0.8	0.5
Mn oxides	0.2	0.1	0.7	0.5
Fe oxides	0.6	0.5	5.3	7.6
Sand	15.4	14.2	7.9	7.3
Silt+clay	79.2	78.2	35.2	54.6

The t_r represents the theoretical time when the highest activity peak of ¹³⁷Cs and ⁶⁰Co appears from soil columns. Because of low GW velocities in the soil columns (Table 2), t_r of radionuclides came up very long. Appearing of highest activity peak corresponding to the travel time of ¹³⁷Cs and ⁶⁰Co through the soil column, it can be said that the length of soil column affects on t_r .

However, differences observed in t_r of both Cs and Co for a given soil are due to porous media sorption capacity, ionic strength of leaching solution, and nature of undisturbed soil columns. The values of travel time calculated by Equation (8) were 411, 1433 days for ¹³⁷Cs, and 100, and 112 days for ⁶⁰Co for loam and clay soils, respectively (Figure 4).

The above results indicate the travel time of Cs was very long compared to Co, and the presence of greater proportion of soil colloids (clay, Fe oxides, and humified organic matter) may increase t_r from hundreds to thousands of years for arbitrary distance of 1000 m because ¹³⁷Cs are more effectively sorbed to the soil colloids. Hossain et al. (2012) found that thickness of soil layer has an effect on t_r of ¹³⁷Cs and ⁶⁰Co through the soil layer. At a given column length (thickness of soil layer) ⁶⁰Co travel time was less comparison with ¹³⁷Cs. The results obtained are consistent with other results given in literature (Meier et al., 2003). This implies that in the presence of soil colloids a large reduction of nuclide

travel times must be taken into account. That is the protective effect of porous media like the soil against the migration of radioactive contaminants to the biosphere can be low in the presence of colloids of soil.

Influence of Leaching with GW on fractionation of ¹³⁷Cs and ⁶⁰Co in soils

Fractionation of Cs and Co in the control samples as well as in samples of the upper 2 cm of both soils columns leached with GW is given in Table 4. For the control soils, it is clearly evident that major portion, 74 to 79% of applied Cs associated with silt+clay. The sand fraction was the second important soil constituent responsible for Cs retention. About 14% of total Cs was retained by the sand fraction in both soils. The retention percent of the Fe oxides was found to be 4.6% for soil 1 and 0.6 for soil 2. The retention percent of organic fraction was 1.3% for both soils. The rest of Cs added was bound to other fractions of soils.

The leaching increased the amount of Cs bound to organic fractions for both soils 1 and 2. Conversely, the exchangeable, carbonate, Mn oxides, and Fe oxides were found to decrease upon leaching. Comparing the fractionation data of Cs from control and soil columns leached with GW for soil 1 (256 g/kg clay) and soil 2 (392 g/kg clay) one can conclude that both soils appeared similar distribution of retaining ¹³⁷Cs.

The fact that the retention percent for two soils are

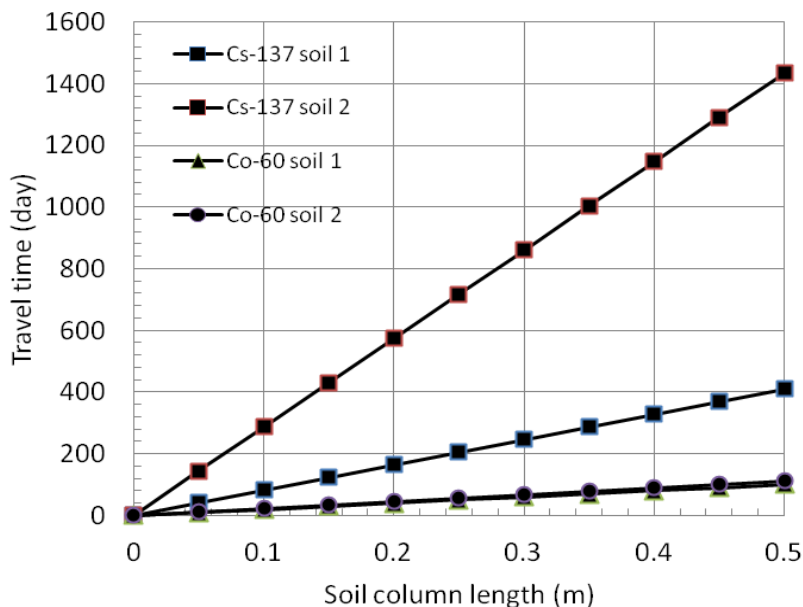


Figure 4. Travel time of ^{137}Cs and ^{60}Co as a function of distance from point of release (soil column length).

similar to each other indicates that the retention of Cs on calcareous soil is mainly determined by the composition of clay minerals. The dominant clay minerals in the two soils are montmorillonite (Table 1), since this type of clay minerals has a high affinity for sorption of Cs. Its affinity for Cs is due to very small hydration energy of the cation and higher electrostatic attraction between Cs and clay particles (Mirkhani et al., 2012). On other hand, the transport of Cs explained the limited replacing ability of the GW because the majority of applied Cs was tightly bound to silt+clay fraction. The amount of Cs released is 75 to 83% over 500 pore volumes using GW as leaching solution (Figures 1 and 2). Also, the K_d of Cs was high in the two soils (Table 2). This may also indicate that fixation (irreversible sorption) was the main mechanism responsible for Cs retention in the soils of montmorillonitic clay. These results are essentially consistent with the results discussed above for transport in soil columns. Bellenger and Staunton (2008) recently observed a strong irreversibility for Cs during desorption experiments from different minerals. Giannakopoulou et al. (2007) showed that clay content plays predominant role on sorption of Cs. Also, the results (Table 4) showed that for the control of both soils, carbonate retained 32 to 47% of ^{60}Co added, although substantial amounts were retained by the clay+ silt minerals, Fe oxides, and sand. Different patterns of Co distribution among soil fractions were obtained for the leached soil columns. The leaching consistently increased the amounts bound to silt+clay minerals, Fe oxides, and water soluble in both soils, whereas it either decreased the amount bound to carbonate (13 to 24%), sand, and Mn oxides fractions (in

the case of soil 1) or slightly changed in the rest fractions. These results are compared with that obtained by others (Razaq et al., 1993; Kamel, 2002) for the release of ^{60}Co from the soil or from the marine sediments. The ^{60}Co radionuclide was bounded to the exchangeable and carbonate fraction. Also, similar results were reported before for Co desorption from soil constitutions (Backes et al., 1995; McLaren and Backes, 1998; Seliman et al., 2012). The amount of Co released out of both soils columns, respectively is 94 and 86% over 300 pore volumes using GW as a leaching solution (Figures 1 and 2). This indicates a smaller degree of reversibility compared to the amounts of Cs released under the same conditions. Also, this may indicates the highest ability of Co to release out of soil columns when it leached with GW compared with Cs.

The results of the present study (Table 4) showed that the substantial amounts of radionuclides especially for ^{137}Cs were retained by sand fraction. It is unexpected to observe this result since the sand is inert component and has small specific surface area. This is may be attributed to fact that sand in arid and semi-arid soils has considerable amounts of light minerals like calcite, feldspar, mica, and quartz which were responsible for Cs and Co retention. Also, the presence of Fe oxides could enhance the adsorption capacity of some minerals (Sipose et al., 2008). From the above results, one can conclude that the behavior of Co is the combined effect of diffusion and development of bound between the nuclide and adsorption sites.

The low replacing ability of GW for release the two radionuclides may due to the fact that ^{137}Cs and ^{60}Co

were found to be influenced by the (i) composition of the soil, (ii) radionuclide characteristics, and (iii) presence of dissolved cations such as Ca, Mg and K in the soil – groundwater system to form coordination bonds. Some researchers attributed the slow desorption process of trace metals from soil constituents surfaces to different mechanisms such as recrystallization of metals into the mineral structure, diffusion into micropores, surface precipitation, change in the surface complex, and solid state diffusion into the crystal matrix (Glover, 2000).

The positive or negative effects on the obtained retention of ^{137}Cs and ^{60}Co data can be supposed mainly of the silt+clay, and sand content of the soil, as well as the carbonate and Fe oxides which especially in the case of ^{60}Co influence this process. Moreover, the very low concentration of tracer radionuclides and carriers, as well as the competition of major ions in the groundwater, including the isotopic exchange between the stable isotope in soil particles and radioactive isotope in the solution has to be considered in the retention of these radionuclides in soil samples (Soderlund et al., 2011).

Conclusions

The convection-dispersion equation (CDE) model allows predicting the transport of ^{137}Cs and ^{60}Co through soil. Also, CDE model provides estimates of the transport parameters of radionuclides. The transport of both radionuclides were slow in soil columns, in spite of the fact that ^{60}Co showed greater mobility than ^{137}Cs . These findings suggest that Cs and Co are strongly retained on soil fractions. The retention may be influenced by several factors, e.g., quantity and quality of clay minerals and other components of the soil. This study also showed that content of silt+clay was associated with the maximum values of K_d , R , and the minimum tr , D , and P .

Most of ^{137}Cs applied was distributed among major soil fractions followed the order silt+clay > sand > organic \geq Fe oxides, while, ^{60}Co was distributed followed the order carbonate > silt+clay > Fe oxides > sand. Leaching however changed either the order or magnitude of fractions. This study exhibits the significance of radionuclides transport features in soil matrix through groundwater flow from the viewpoints of safety aspects of surface level disposal facility. Current risks appear to be low because such calcareous soils will tend to retain the large amount of radionuclides which might release from the burial site and reduce the potential migration of radionuclides to the environment. More thorough investigations regarding long-term is required to accurately estimate the amount of risk associated with contamination from the site.

Conflict of Interest

The authors have not declared any conflict of interest.

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