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# DIFFUSION-SORPTION EXPERIMENT FOR STUDYING TRANSPORT PROPERTIESOF $^{137}Cs$ AND $^{85}Sr$ IN SOIL

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**Abstract.** The radionuclides released from nuclear weapon tests during the 1960's and from nuclear industries may still endanger the terrestrial environment. Therefore, a diffusion-sorption experiment has been carried out to study the behaviour of the radionuclides that are of interest in safety assessments in the environmental radioactivity field such as $^{137}Cs$ and $^{90}Sr$. The systems studied were as close as possible to those encountered in the field. The experimental data were evaluated by numerical analysis, incorporating linear and nonlinear sorption models (six sorption isotherm models). This procedure enables us to calculate the sorption parameters of different sorption isotherm models.

The parameters determinated were the diffusion and sorption properties of cesium and strontium in an Orthic Podsol soil (Germany).

## I. Introduction

It is well recognized that many radionuclides, particularly the cationic species migrate slowly as a result of interaction of radionuclides with the soil matrix. Among radionuclides, $^{137}Cs$ and $^{90}Sr$ belong to the most hazardous radionuclides due to their long halflives and their low migration rates (of the order of 1 cm per year [1]). This implies that after many years, they still remain within the root zone of the soil where they can be taken up by plants and later could reach the ground water. As a consequence, they transfer into human food chains and drinking water. Therefore, it is important to understand the transport process of $^{137}Cs$ and $^{90}Sr$ in the soil matrix.

There are various laboratory methods for studying transport of radionuclides in soil, such as the batch method and the column method. The main advantage of the batch method is its simplicity. However, there are also several disadvantages: not all hydrologic flow effects are counted, the ratio of the solution to the solid is higher (due to experimental necessities), and higher sorption capacities may be available for tracer due to the shaking process. Hence, because of the experimental conditions (which differ from those in the field) this method may give inaccurate result [2]. The column method can eliminate these disadvantages. Its major disadvantage is its complexity and that it is very time- consuming [3-4].

The work presented here applies a different method for studying transport of cesium and strontium in soil, the modified diffusion-sorption experiment. In the present study, $^{90}Sr$ has been substituted by $^{85}Sr$ which is chemically identical, has a considerably shorter halflife and can be detected more easily. The aims of the work are to:

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Determine diffusion and sorption parameters for $^{137}Cs$ and $^{85}Sr$

Sorption models (linear, Langmuir, Freundlich) are tested by fitting the experimental data.

## II. Experimental procedure

The diffusion-sorption experiment was performed using Orthic Podsol soil consisting of 96.2% sand, 3.1% silt and 0.7% clay. It is a typical soil in North Germany [1]. $^{137}Cs$ (cesium chloride in 1N HCl) and $^{85}Sr$ (strontium chloride in aqueous solution) were used as tracers. The tracer solution was prepared by adding some synthetic solution to the acid solution containing the radionuclides. Initial tracers concentrations, Co in the reservoir cell were about 70 k Bq/l.

The arrangement for the diffusion-sorption experiment is illustrated in Fig.1.

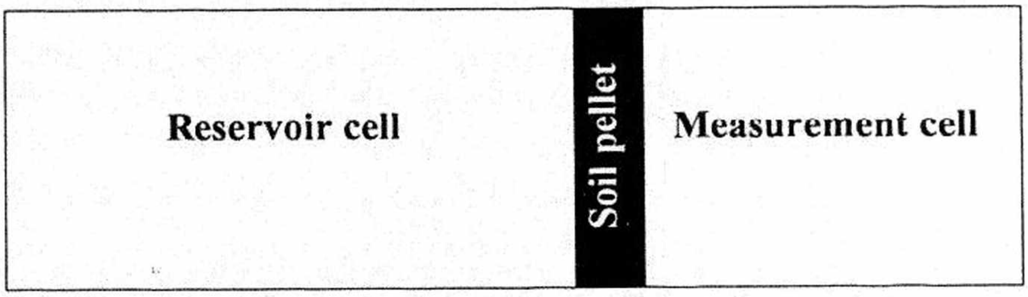

*Fig.1.* Experimental set-up for the diffusion-sorption experiment

The soil pellet was a disk with a diameter of 1.78 cm and a thickness of 0.4 cm. The dimensions of the soil pellet were 2.49 $cm^2 \times$ 0.4 cm. Porosity and density of the soil pellet were 36% and 1.70 ± 0.01 g $cm^{-3}$, respectively. The soil pellet was fixed between two cells, the reservoir cell of 490 ml containing the tracers and the measurement cell of 230 ml containing synthetic soil solution. The concentrations Co (t) of tracers in the reservoir cell were allowed to decrease with time by the amount diffused into soil pellet, also by the decay of the tracers. In the measurement cell samples were withdrawn at certain intervals. The fluid of the measurement cell was replaced by the synthetic soil solution, maintaining a near-zero concentration. A synthetic solution was selected containing element concentrations which are as close as possible to the values calculated from the analyses of the soil solution sample in the field. Tracers diffuse from high to low concentration.

The experiment was performed at room temperature of $20^0$C. $^{137}Cs$ and $^{85}Sr$ concentrations in solution samples were detected by high purity germanium- detector. Statistical counting errors were in the range of 1÷5%.

## III. Data analysis

Assuming a single-porosity medium, in which the diffusion coefficient D is constant in time and space, transport (diffusion is accompanied by sorption) in the liquid phase can be described by a one-dimensional equation

$$\frac{\partial(x,t)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2} - \frac{\rho}{\epsilon}\frac{\partial S(x,t)}{\partial t}, \qquad (tgeq0, 0 \leq x \leq L), \tag{1}$$

where $C$ : concentration of trace in solution;

$S$ : concentration of trace sorbed;

$\rho$: soil density;

$\epsilon$ : soil porosity;

$D$ : effective diffusion coefficient;

$L$ : length of soil pellet.

For our experimental arrangement, initial conditions are given as

$$C(x,0) = \begin{cases} C_0, & x = 0, \\ 0, & x > 0. \end{cases} \tag{2}$$

And the boundary conditions are [3]

$$C(0,t) = C_0 - \int_{\tau=0}^{t} \frac{\partial C(0,\tau)}{\partial \tau}, \tag{3}$$

$$C(L,t) = 0. \tag{4}$$

According to Fick's law eq. (3) may be written as

$$C(0,t) = C_0 + \frac{A}{V}\int_{\tau=0}^{t} \epsilon D \left(\frac{\partial C(c,\tau)}{\partial x}\right)_{x=0} d\tau. \tag{5}$$

The sorption of the tracer to the soil matrix is modelled by a non-linear first order kinetic model

$$\frac{\partial S}{\partial t} = r\{F(C) - S\}, \tag{6}$$

where $r$ : kinetic time constant;

$F(C)$ : sorption isotherm.

No analytical solution is known for this problem; solutions are obtained by numerical method. This is performed by using Crank-Nicolson method of a finite difference and solving the resulting system of nonlinear difference equations by Newton-Raphson method. This was described in more detail by G. Kirchner, [3]. The numerical algorithms were built into the nonlinear code PAR of the BMDP statistical code package (BMDP statistical software W. J. Dixon, [5]).

Akaike information criterion AIC can be used to fit the sorption models to experimental data. *Criteria* based on Akaike information criterion AIC if measurement errors are additive and normally distributed with mean zero it is given as C. Cobeli, [6].

$$AIC = N \ln R_{SS} + 2p,$$

where $N$ : number of data points;

$R_{SS}$ : residual sum of squares of the fit;

$p$ : number of parameters fitted.

According to the test, the sorption model with the lowest value of $AIC$ is considered the best, taking into account the goodness of the fit as well as and number of the parameters fitted.

## IV. Results and discussion

The sorption models listed in tab. 1 were fitted to the experimental data for ${}^{85}Sr$ and ${}^{137}Cs$ with the linear, Freundlich, and Langmuir isotherm assuming instantaneous and first order kinetic sorption, respectively. The differential equation thus obtained can be applied as a regression model with $D, r, K_d, K_{Fr}, K_{La1}, K_{La2}, N$ as fitting parameters.

The table 1 shows sorption models fitted to the experimental data of ${}^{85}Sr, {}^{137}Cs$ and the obtained values of $AIC$ and $R_{SS}$.

**Tab.1** Testing the fits of the sorption models for ${}^{85}Sr$ and ${}^{137}Cs$ using the Akaike criterion

| No | Sorption model | ${}^{85}$Sr | | ${}^{137}$Cs | |
|---|---|---|---|---|---|
| | | $R_{SS}$ | AIC | $R_{SS}$ | AIC |
| 1 | $S = K_d . C$ | 116571 | 678 | 38955 | 1050 |
| 2 | $S = K_{Fr} C^N$ | 116572 | 680 | 37722 | 1049 |
| 3 | $S = \frac{K_{La1} C}{1 + K_{La2} C}$ | 116576 | 680 | 38954 | 1052 |
| 4 | $\frac{\partial S}{\partial t} = r\{K_d C - S\}$ | 116575 | 680 | 34353 | 1040 |
| 5 | $\frac{\partial S}{\partial t} = r\{K_{Fr} C^N - S$ | 116881 | 684 | 34388 | 1042 |
| 6 | $\frac{\partial S}{\partial t} = r\left\{\frac{K_{La1} C}{1 + K_{La2} C} - S\right\}$ | 72027 | 813 | 34353 | 1042 |

As can be seen from tab. 1, the best fit to the experimental data for ${}^{85}Sr$ and ${}^{137}Cs$ were obtained assuming a linear isotherm and a kinetic linear isotherm, respectively.

Parameters resulting from fitting the sorption models for the linear isotherm of ${}^{85}Sr$ and for the kinetic linear isotherm of ${}^{137}Cs$ are given in tab. 2.

**Tab.2.** Parameters obtained by fitting the experimental data of ${}^{85}Sr$ and ${}^{137}Cs$, where the uncertainties of the values were derived from the asymptotic standard deviations.

| Parameter | Numerical value | |
|---|---|---|
| | ${}^{85}$Sr | ${}^{137}$Cs |
| D ($10^{-3}$ cm$^2$ h$^{-1}$) | 10.1 ± 0.6 | 29.6 ± 1.1 |
| $K_d$ ( cm$^3$ g$^{-1}$) | 7.4 ± 1.3 | 50.7 ± 13.3 |
| r ($10^{-6}$ s$^{-1}$) | instantaneous | 1.36 ± 0.47 |

The experimental data of strontium and cesium concentrations diffused into the measurement cell and the fitted curves obtained from the regression analysis are shown in figure 2 and 3, respectively.

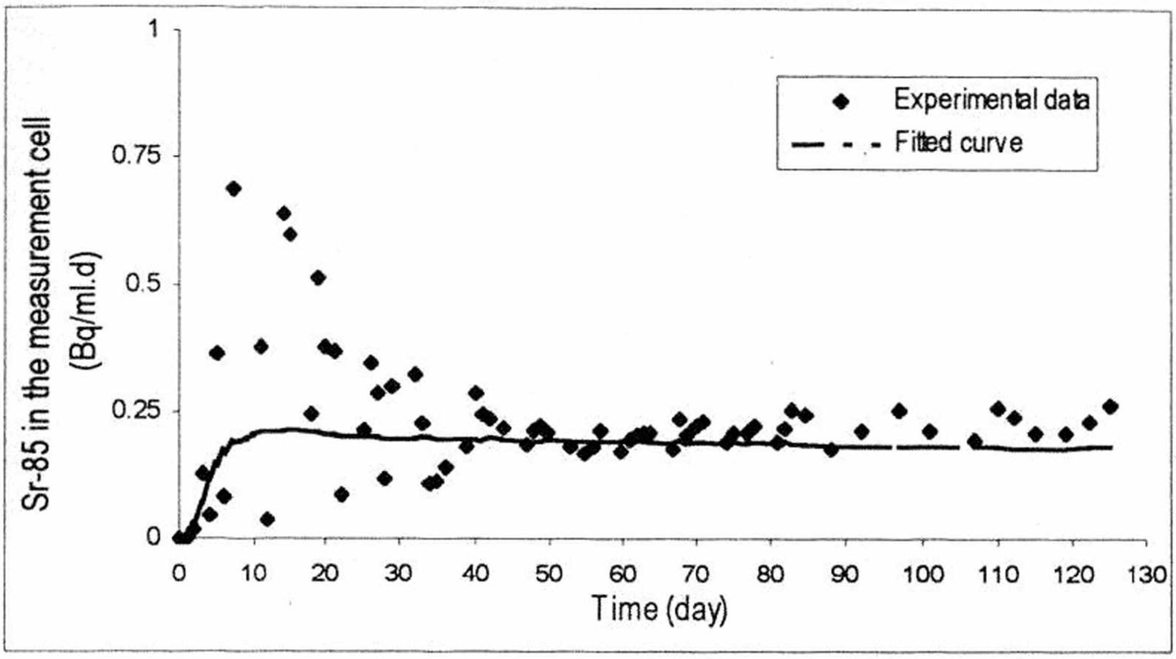

*Fig.2* Concentrations of $^{85}Sr$ diffused into the measurement cell in 1 day-intervals during the experiment compared to the fit of a linear sorption model

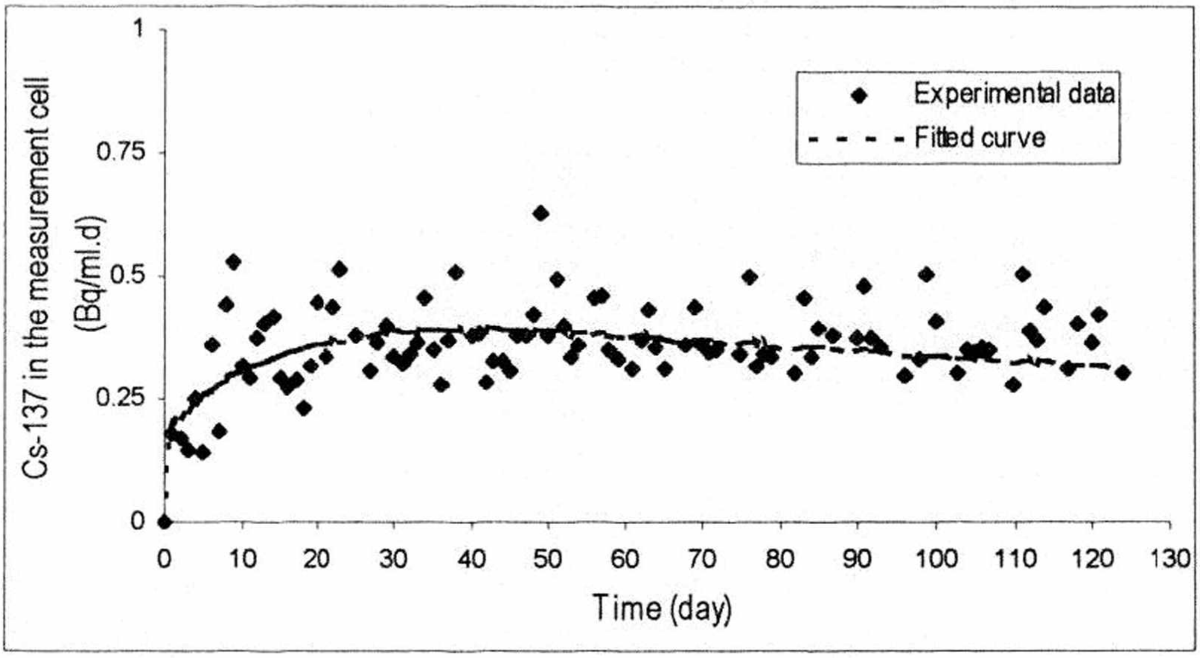

*Fig.3* Concentrations of $^{137}$Cs diffused into the measurement cell in 1 day-intervals during the experiment compared to the fit of a kinetic linear sorption model

As can be seen in figures 2 and 3, the calculated curves are in satisfactorily agreement with the experimental data for both strontium and cesium. The strontium data have been corrected for its decay, since the half-life of $^{85}Sr$ is 65 days. The uncertainties of the values of the effective diffusion coefficients are below 6%. The high uncertainties of obtained sorption parameter may result in large errors on individual data points due to the variation of the concentrations of cesium and strontium diffused into the measurement cell.

The results show that the sorption isotherms for both strontium and cesium are linear.

The interaction kinetics for strontium to the soil matrix is a fast process while the kinetic sorption for cesium is slow. From the value of r $(1.36 \pm 0.47)*10^{-6}$ $s^{-1}$, the reaction time of cesium $\tau = \ln 2/r$ can be calculated to be 6 days. This result is in good agreement with corresponding values in the literature [7-11].

The wide range of $K_d$-values reported in the literature, up to three order of magnitude and more [12], is due to the different geochemical factors of the various materials used. However, our results are similar to those of similar soil and tracer concentrations found by some authors [7,12-14].

In conclusion, diffusion-sorption experiments have a number of advantages such as their experimental simplicity and the possibility to model conditions that are close to those in the field and therefore give accurate results.

Although the determination of the migration rate of strontium and cesium in soil will be the subject of another study, we can give a rough estimate of the migration of radionuclides in soil. Diffusion is dominant when the fluid velocity is of the order of 5 cm per year. In the case of linear sorption, the distribution coefficient can be used as rough estimate to predict the migration of radionuclides in soil which can be described as:

$$l = \sqrt{2\epsilon Dt/R_d}$$

where:

$$R_d = 1 + \frac{\rho}{\epsilon} K_d.$$

Using the results of our experiment, the migration of 1 m of either strontium or cesium in Podsol soil can be estimated to take about 100 (more or less) years during which the activity would be reduced by a factor of 10. Therefore, it is of interest to get information on the migration and sorption of strontium and cesium in various materials (soil, rock...) in order to allow a safety analysis in the environmental radioactivity field.

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