Modeling of $^{137}$Cs Migration from Soil to Plants after Usage of Chemical Matters

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Abstract

A mathematical model of $^{137}$Cs migration from soil to plant is improved. An expression for the parameter of $^{137}$Cs migration in soil was received, which is a combination of parameters of soil solution (concentration of $^{137}$Cs and Ca$^{2+}$) and which allows to predict the coefficient of $^{137}$Cs accumulation in plants and estimate the efficiency of different methods for reducing of $^{137}$Cs migration from soil to plants. It is shown that the parameter of migration, calculated on the basis of parameters of soil solution is linearly related with the coefficient of $^{137}$Cs accumulation from soil to plants. The model was validated with the use of a set of experimental data obtained in vegetation experiments. The assessment of the effect of potassium fertilizer (KCl) on $^{137}$Cs migration from soil to plant was carried out.

Key words: cesium, soil, migration, modeling, mathematical model, parameter of migration.

1. Introduction

The main indicator of risk for the population living on the contaminated territories is a radiation dose. Numerous studies of national and international researchers show that the maintaining of agricultural production in terms of radioactive contamination of the soil in Belarus after the Chernobyl accident the main source of internal exposure is $^{137}$Cs. Traditionally, for describing of $^{137}$Cs migration from soil to agricultural crops the concentration factor (CF) was used. However, the practical use of CF for dose and risk assessment encounters certain difficulties associated with its great variability depending on the physical and chemical properties of soil and plant species. Thus, the multiplicity of...
The same plant species growing on different soil types can be up to several orders of magnitude higher in their ability to take up 

As a solution to this problem, a mathematical model can be developed, which takes into account the influence of physical, chemical, and biological processes on the migration of 

The object of the mathematical modeling is a system consisting of a solid phase of the soil, soil solution, and plants. To assess the effect of chemical substances (potassium) on the 137Cs transfer from soil to plants potassium chloride (KCl) is used. For experimental verification of the mathematical model, it is used a set of data obtained in pot experiments with soddy-podzolic soils. Soil preparation, application of 137Cs, and the insertion of different doses of KCl in the soil, plant selection and planting, watering, and the allocation of the soil solution were performed as described in paper 2. Activity of 137Cs in the soil, soil extracts, and plant material were determined by scintillation gamma spectrometry device RUS-91M, ion content of $K^+$, $Ca^{2+}$, $Mg^{2+}$ in the soil solution – by atomic absorption spectrophotometry (Vario Spectr AA250). The measurement results were processed using mathematical statistics software Statistica-6 and MS Excel 2007.

The migration of 137Cs from soil to plant is determined by the characteristics of its behavior in the solid phase of the soil – soil solution – a plant. In this context, in various models [1, 3–6] a complex process of ions absorption by plants from the soil is broken into two main stages:

1. distribution of ions between the solid and liquid (soil solution) phases of the soil;
2. ion uptake by plant roots from the soil solution.

Respectively, two levels of regulation of the migration of 137Cs in the soil – soil solution – a plant are defined:

1) the level of soil (soil – soil solution), quantitatively characterized by the exchange ratio of the distribution ($K_{d_{\text{ex}}}$);
2) biological (or physiological) level (soil solution – plant), estimated by CF, which is largely determined by the concentration of the ions $K^+$, $NH_4^+$, $Ca^{2+}$, $Mg^{2+}$ in soil solution.

Processes and reactions that take place in the soil – soil solution and which have a physical and chemical nature, determine the mobility of 137Cs and its potential availability for uptake by plant roots. The mechanisms and processes of ions transport through biological membranes while their uptake by roots and their subsequent migration to the plant are connected with the regulation on the biological level. Ion absorption plays an important role in the whole process of 137Cs migration from soil to plant, because 137Cs is not a mineral nutrition element for the plant, but it is transferred by transportation systems of its macroanalogue $K^+$ [7].

Thus, the migration of 137Cs from soil into the plant is determined by superposition of various physico-chemical and biological processes, the formalization of which is possible only in the framework of mathematical models. In papers [1, 3–6] there are proposed mathematical models of various difficulty which describe the transfer of 137Cs from soil to plant. The core of these models is the assumption that the radionuclide 137Cs in the soil solution is in the dynamic equilibrium with the two ion exchangers – the solid phase of the soil and the root of the exchange complex (plant roots). Comparative evaluation of mathematical models of 137Cs migration from soil to plant [1, 3–6] based mainly on the number of indicators included in these models, and their experimental determination shows that the model described in the paper in [4], is the most preferred for the forecast of 137Cs migration from soil to plant.

According to the mathematical model [4], the CF is a linear function of the parameter of the biological availability of 137Cs:

$$CF = kA$$  \hspace{1cm} (1)
$k$ – coefficient of proportionality between the amount of $^{137}\text{Cs}$, absorbed by the plant, and its share in the root exchange complex which characterizes the efficiency of transfer of $^{137}\text{Cs}$ through the membrane of the plant cell;

$A$ – parameter of bioavailability of $^{137}\text{Cs}$ in the soil.

Parameter of bioavailability is determined according to the following formula:

$$A = \frac{\alpha_{ex}}{\text{RIP}^{ex}(K)} \times \frac{\text{PNAR}^{ex}}{\text{RIP}^{ex}(K)} \times \left( 1 + K_c(\text{NH}_4^+/K^+) \frac{[\text{NH}_4^+]_w}{[K^+]_w} \right) \frac{\text{PAR}}{\text{K}} \quad (2)$$

Where,

$\alpha_{ex}$ – the content of exchangeable form of $^{137}\text{Cs}$, which characterizes the fixing ability of the soil;

$\text{RIP}^{ex}(K)$ – Radiocaesium Interception Potential (potential of selective sorption for cesium), meq/kg;

$\text{PNAR}$ – potassium and ammonium adsorption ratio, (mmol/l)$^{1/2}$;

$K_c(\text{NH}_4^+/K^+)$ – selectivity factor $\text{NH}_4^+$ relative to $K^+$ in ion-exchange on selective sorption centers FES (Frayed Edge Sites);

$[\text{NH}_4^+]_w$, $[K^+]_w$ – the concentration of the respective cations in the soil solution, mmol/l;

$\text{PAR}$ – potassium adsorption ratio, (mmol/l)$^{1/2}$, calculated from the ratio:

$$\text{PAR} = \frac{[K^+]_w}{\sqrt{[\text{Ca}^{2+}]_w + [\text{Mg}^{2+}]_w}} \quad (3)$$

Where,

$[K^+]_w$, $[\text{Ca}^{2+}]_w$, $[\text{Mg}^{2+}]_w$ – concentration of cations in the soil solution corresponding, mmol/l.

When analyzing the bioavailability of $^{137}\text{Cs}$ under definite conditions, formula (2) can be simplified [4]. Thus, for most types of soil in the soil solution $[K^+]_w \gg [\text{NH}_4^+]_w$, the following formula is obtained:

$$A = \frac{\alpha_{ex}}{\text{RIP}^{ex}(K)} \frac{\text{PNAR}}{\text{K}}. \quad (4)$$

The main disadvantage of the mathematical model described in paper [4], as well as other models [1, 3, 5, 6], is the use the content of $^{137}\text{Cs}$ exchangeable form ($\alpha_{ex}$), for calculating of CF. Standard procedure for determining of the exchange form of $^{137}\text{Cs}$ in soil is its extraction by ammonium acetate solution (concentration of 1 mol/l, pH = 7). However, in the natural soil solutions such high salt concentrations practically do not occur. In mineral soils the basic mechanism of selective sorption of $^{137}\text{Cs}$ is an ion exchange of $^{137}\text{Cs}$ for $K^+$ and $\text{NH}_4^+$ at FES (which is selective to cesium) within the wedge-shaped edges of clay minerals such as illite. As it is known from the paper [8], the use of such concentrated salts can cause collapse of the clay minerals inter-packet spaces, whereby $^{137}\text{Cs}$, located therein, is unable to pass into solution. In connection with this fact, the measured share of exchange $^{137}\text{Cs}$ can be much smaller than it actually is. Therefore, the use of $\alpha_{ex}$ to predict $^{137}\text{Cs}$ migration from soil to plant raises serious doubts.

On the other hand, as shown in the paper [9], isolation of radionuclides by centrifugation directly from the soil solution at 60% soil moisture of total moisture capacity that substantially corresponds to their natural moisture conditions, provides a high degree of correlation between the radionuclide content in the soil solution, and their availability to plants. For elimination of these contradictions the following formulas are in use:

$$[^{137}\text{Cs}^+]_{ex} = \alpha_{ex} [^{137}\text{Cs}] \quad (5)$$

$$\frac{[^{137}\text{Cs}^+]_{ex}}{[^{137}\text{Cs}^+]_w} = K_c(\text{Cs}^+/K^+) \frac{[K^+]_{ex}}{[K^+]_w} \quad (6)$$
The method of rehabilitation of agricultural soils contaminated with radionuclides of Cs and K obtained in the course of pot experiments with soddy-podzolic soils (sandy and sandy loam), and the same plant (barley) using the method which in the paper [2]. To simulate the impact of potash fertilizers on the process of 137Cs migration from soil to plant in increasing doses from 20 to 100 mg/kg, K+ was inserted to the soil in the form of KCl. The use of KCl is regarded as a major method of rehabilitation of agricultural soils contaminated with radionuclide 137Cs [12].

\[ K_{ex}^{\text{K}} = \frac{[\text{Cs}^{+}]_{\text{ex}}^{137}}{[\text{K}^{+}]_{\text{w}}^{137}} \]  

(7)

\[ \text{RIP}^{137}(\text{K}) = K_{ex}^{\text{K}}[\text{K}^{+}]_{\text{w}} \]  

(8)

Where,  

\[ [\text{Cs}^{+}]_{\text{ex}}^{137}, [\text{K}^{+}]_{\text{ex}}^{137} – \text{concentration of cations in the solid phase of the soil corresponding, meq/kg;} \]  

\[ [\text{Cs}]^{137} – \text{the total concentration of radionuclide in the soil, Bq/kg;} \]  

\[ [\text{K}^{+}]_{\text{w}}^{137} – \text{concentration of cesium in soil solution, Bq/l;} \]  

\[ [\text{K}^{+}]_{\text{w}} – \text{concentration of potassium in soil solution, mmol/l;} \]  

\[ K_r(\text{Cs}^{+} / \text{K}^{+}) – \text{coefficient of Cs\textsuperscript{+} selectivity with respect to K\textsuperscript{+} during ion exchange at FES;} \]  

\[ K_{ex}^{\text{K}} – \text{exchange distribution coefficient of 137Cs between solid phase and soils solution, l/kg.} \]

After appropriate transformations using the formulas (4)–(8) the following is obtained:

\[ A = \frac{[\text{Cs}^{+}]_{\text{w}}^{137}}{[\text{K}^{+}]_{\text{w}}^{137}} \frac{[\text{K}^{+}]_{\text{w}}}{\sqrt{[\text{Ca}^{2+}]_{\text{w}}^{137} + [\text{Mg}^{2+}]_{\text{w}}^{137}}} \]  

(9)

Where the ratio \( \frac{[\text{Cs}^{+}]_{\text{w}}^{137}}{[\text{K}^{+}]_{\text{w}}} \) is determined by the physical and chemical processes of the sorption and desorption of 137Cs in the soil solid phase and depends on the cation composition of the liquid phase of the soil and \( K_r(\text{Cs}^{+} / \text{K}^{+}) \), and the ratio \( K_r(\text{Ca}^{2+} / \text{K}^{+}) \) determines the equilibrium fraction of 137Cs in the root of the exchange complex.

Equation (9) can be simplified by neglecting a content of [Mg\textsuperscript{2+}] in the soil solution. First, the content of [Mg\textsuperscript{2+}] in the majority of soils is less than 20% of the content of [Ca\textsuperscript{2+}] and, secondly, the selectivity of Ca\textsuperscript{2+} during the exchange at the root exchange complex of plants is 2–3 times higher than Mg\textsuperscript{2+} [10]:

\[ A = \frac{[\text{Cs}^{+}]_{\text{w}}^{137}}{[\text{Cs}]^{137}} \frac{1}{\sqrt{[\text{Ca}^{2+}]_{\text{w}}^{137}}} \]  

(10)

The quality of 137Cs migration from soil to plant is largely dependent on the absolute concentration of K\textsuperscript{+} in soil solution. At low concentrations (< 0.3 mmol/l), potassium greatly impedes the flow of 137Cs into the plant. When K\textsuperscript{+} concentration is above 1 mmol/l, the change of its content in the soil solution is only slightly affects the migration of 137Cs to the plant [10]. The formula (10) for calculating the parameters of 137Cs migration is applicable to any concentration of K\textsuperscript{+} (KCl) in the soil solution which do not cause inhibition of growth and development of plants.

The analysis of the formula (9) shows that one of the ways of reducing the bioavailability of 137Cs is application of chemical substances (potassium, and dolomite) into soil, causing changes in the composition of the soil solution, and, therefore, root feeding of plants. Another way is the insertion into soils of sorbents capable of non-exchange sorption of water-soluble forms of 137Cs and at the same time increasing the capacity of the ratio (FES) of the contaminated soils.

4. Comparison with experimental data

For experimental verification of the model it was used a set of data (one's own and of other authors [2, 11]) obtained in the course of pot experiments with soddy-podzolic soils (sandy and sandy loam), and the same plant (barley) using the method which in the paper [2]. To simulate the impact of potash fertilizers on the process of 137Cs migration from soil to plant in increasing doses from 20 to 100 mg/kg, K\textsuperscript{+} was inserted to the soil in the form of solutions of KCl. The use of KCl is regarded as a major method of rehabilitation of agricultural soils contaminated with radionuclide 137Cs [12].
As it is known, $^{137}$Cs does not form any stable complex compounds and in the soil solution is mainly in the form of cations [13]. Changing of the content of $^{137}$Cs in the soil solution is conditioned by the non-selective and selective sorption of this radionuclide at clay minerals. Release of further quantities of potassium into the soil solution initiates the ion exchange processes, leading to the increase of $^{137}$Cs migration to the solution [14]. On the other hand, if at the selective centers FES a sufficient amount of K$^+$ cations is sorbed, it can cause a collapse of illite-type minerals with the laminated-type structure [15], which leads to fixation of $^{137}$Cs therein and simultaneously $^{137}$Cs loses its ability to exchange with other cations (K$^+$, NH$_4^+$).

In soils with optimum potassium content the layered minerals have already been significantly subjected to a collapse. Therefore, the impact of increasing concentrations of K$^+$ on the fixation of $^{137}$Cs is less pronounced and the ability of K$^+$ ions to compete with $^{137}$Cs for FES centers becomes more significant. Despite the fact that the relationship between $^{137}$Cs and FES of clay minerals is strong enough, the excess of K$^+$ ions in the soil can damage it [16].

The following Table 1 shows the effect of potassium on the accumulation of $^{137}$Cs by barley seedlings and the characteristics of soil solutions (outlined as described in the paper [2]) of the soil used for calculation of the parameter of $^{137}$Cs ($A_{137}$) migration (bioavailability).

<table>
<thead>
<tr>
<th>Soil type</th>
<th>Number K$^+$ introduced into the soil, mg/kg</th>
<th>pH$_{KCl}$</th>
<th>The concentration of cations in the soil solution, mmol/l</th>
<th>The specific activity of $^{137}$Cs, kBq/l</th>
<th>CF($^{137}$Cs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soddy-podzolic sandy [2, 11]</td>
<td>0</td>
<td>5.8</td>
<td>0.03</td>
<td>3.50</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>5.8</td>
<td>0.34</td>
<td>3.50</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>5.7</td>
<td>1.84</td>
<td>6.90</td>
<td>0.82</td>
</tr>
<tr>
<td>Soddy-podzolic sandy loam</td>
<td>0</td>
<td>5.5</td>
<td>0.09</td>
<td>4.02</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>5.5</td>
<td>0.21</td>
<td>4.05</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>5.5</td>
<td>0.30</td>
<td>4.08</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>5.5</td>
<td>0.45</td>
<td>4.11</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>5.4</td>
<td>1.91</td>
<td>8.51</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>5.4</td>
<td>2.52</td>
<td>9.12</td>
<td>0.67</td>
</tr>
</tbody>
</table>

The Fig. 1 shows the dependence of CF $^{137}$Cs for barley seedlings from the parameter of migration ($A$), calculated according to the formula (10).

![Graph showing the dependence of CF for $^{137}$Cs from $A$ for barley seedlings](image)

**Fig. 1:** The dependence of CF for $^{137}$Cs from $A$ for barley seedlings
It can be seen that with the increase of $A$ an increase of the CF occurs. The correlation coefficient ($R^2$) for a line passing through the origin of coordinates is 0.934. Linear regression equation for barley seedlings is as follows:

$$\text{CF} = 4.08A$$ (11)

Coefficient of the linear regression equation determines the angle of inclination of the line (figure), which depends on the biological characteristics of the plant. Results of the comparison of experimental and calculated dependences show that the formula (10) accurately describes the transfer of $^{137}\text{Cs}$ from soil to plant.

5. Conclusion

The mathematical model based on the identification of the mechanisms that control the physico-chemical and biological processes which together determine the migration of $^{137}\text{Cs}$ from soil to plant is improved. It was established a formula (10) for the parameter of $^{137}\text{Cs}$ migration in the soil, which is a combination of key indicators of the soil solution. It is shown that the parameter of bioavailability calculated on the basis of the soil solution parameters, is linearly related to the coefficient of $^{137}\text{Cs}$ accumulation during its migration from a soil to plants.

The model is tested using a set of experimental data obtained in pot experiments. On the basis of the performed assessment of the impact of the chemical substance ($\text{KCl}$) on the $^{137}\text{Cs}$ migration from the soil into barley seedlings it was found that the introduction of $K^+$ at a dose 100 mg/kg into sandy and sandy loam soils reduces about twofold the migration of $^{137}\text{Cs}$ from these soils to plants.

The formula (10) for the determination of $^{137}\text{Cs}$ migration (bioavailability) in the soil allows to forecast of $^{137}\text{Cs}$ accumulation factor in plants on the basis of indicators of soil solution (concentrations of $^{137}\text{Cs}$ and $\text{Ca}^{2+}$) and to assess the effectiveness of different sorbents to reduce the migration of $^{137}\text{Cs}$ from soil to plant. The advantage of this model is that it has a small number of parameters which have a clear physical meaning and may be determined by standard physico-chemical methods.

References


