Modelling of ^{137}Cs behaviour in the soil-plant system following the application of ameliorants

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Abstract. A set of countermeasures aimed at reducing ^{137}Cs uptake by plant products includes agrochemical measures based on changes in the soil properties after the application of ameliorants. The dynamic models for studying the effect of the application of potassium fertilizers and dolomite powder on ^{137}Cs accumulation in plants are presented. Conceptual approaches to the development of models are based on the identification of mechanisms governing a complex of physico-chemical processes in soil after the use of ameliorants. The developed models were parameterized for soils of the coniferous forest located in the Bryansk region in area suffered from the radioactive fallout after the Chernobyl accident. Effects of ameliorants and time of their application on ^{137}Cs behaviour in the soil-plant system are assessed. The contribution of soil chemical and biological processes to the decrease in the radionuclide uptake by plants is estimated.

1. INTRODUCTION

A large-scale contamination of agricultural and forest ecosystems with long-lived radionuclides after the Chernobyl accident has resulted in the need for the development of countermeasures to reduce the accumulation of radionuclides in farm and forest products. A set of countermeasures aimed at reducing ^{137}Cs uptake by plant products includes agrochemical measures based on changes in the soil properties after the application of ameliorants. Among the ameliorants recommended for use in the affected areas are potassium fertilizers and dolomite powder [1], after the application of which extra amounts of K^+ and Ca^+ cations are taken in the soil solution. The dynamics of ^{137}Cs uptake by plants following the use of ameliorants is determined by the superposition of different physico-chemical and biological processes. However, formulating of these processes is only possible by mathematical modelling. The objective of the present paper is to develop dynamic models for studying the effect of the application of K fertilizers and dolomite powder on ^{137}Cs accumulation in plants. Conceptual approaches to the development of models are based on the identification of mechanisms governing a complex of physico-chemical processes in soil after the use of ameliorants.

2. CONCEPTUAL APPROACHES

Fig.1 shows a conceptual scheme of the model, which reflects ^{137}Cs behaviour in the soil-plant system after the application of K fertilizers. The model describes ^{137}Cs distribution by its species in each soil layer and vertical migration of this radionuclide. Variations in ^{137}Cs content in soil solution are caused by the nonselective and selective sorption of this radionuclide on clay minerals. Selective sorption sites (FES) are located on expanded end sites of interlayer spaces of stratified clay minerals, whereas nonselective sorption centers (RES) are on the surface of soil particles [2]. Since FES is characterized by high selectivity with respect to ^{137}Cs cations and other univalent cations (K^+, NH_4^+), bivalent cations do not complete with them for FES sites. In the course of time fixation of univalent cations (including ^{137}Cs) in the crystal lattice occurs [3].

The uptake of extra amounts of potassium in the soil solution induced intensification of ion exchange processes and increases ^{137}Cs transfer to solution. On the other hand, high content of potassium initiates an effect of interlayer collapse in the layers of clay mineral crystal lattice, resulting in enhanced ^{137}Cs fixation. The application of dolomite powder leads to a rise in Ca^{+} concentration in soil solution. Bivalent Ca^{+2} cations are not capable of penetrating inward the wedge-shaped zone, causing its stabilization – retaining it in a dilated state, as a result of which added amounts of ^{137}Cs cations occupy FES sites. With the decline in Ca^{+2} concentration in soil solution, due to vertical migration and other processes in soil, layer collapse of clay minerals ("delayed collapse") is intensified and, consequently, ^{137}Cs fixation is increased in the crystal lattice.
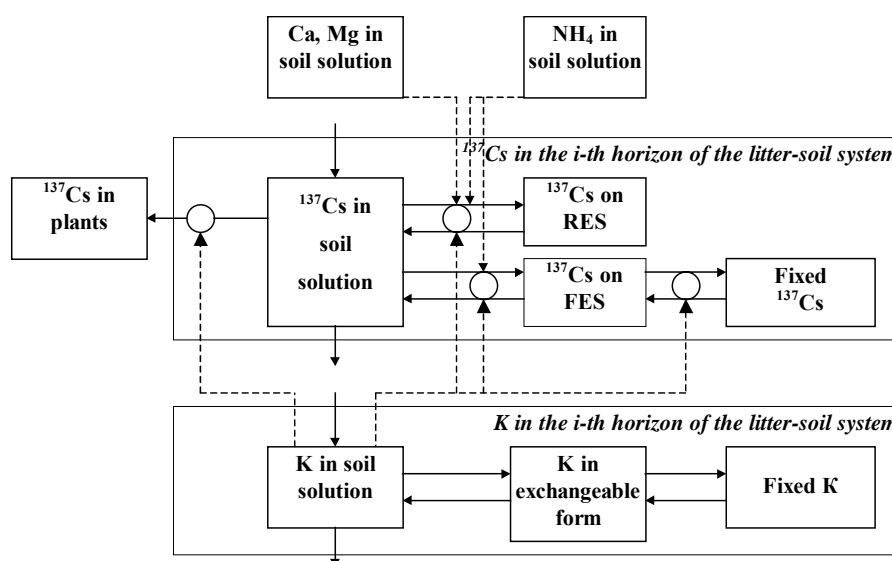
Figure 1. A conceptual scheme of the model describing effect of K fertilizing on ^{137}Cs behaviour in the soil-plant system.

The following assumptions were used in the development of models:

- dynamics of ^{137}Cs distribution in each soil layer depends on the sorption processes characterized by different time to achieve quasi-equilibrium (exchangeable uptake and fixation by clay minerals) as well as on vertical migration process;
- change in ^{137}Cs content in soil solution results from the radionuclide sorption on selective and nonselective exchange sites;
- uptake of extra amounts of K^{+} and Ca^{2+} in soil solution produces effect on processes of ^{137}Cs exchangeable sorption and initiate specific processes responsible for ^{137}Cs fixation in the crystal lattice of clay minerals;
- Ca^{2+} and K^{+} cations have a competing effect on ^{137}Cs uptake by plants from soil solution, which along with the fixation processes causes lower accumulation of this radionuclide by plants during the application of ameliorants.

3. MATHEMATICAL REALIZATION OF MODELS

The ^{137}Cs content in soil components is described by a set of variables, which have dimensions of Bq m^{-2}. The processes of ^{137}Cs exchangeable sorption on selective and nonselective exchange centers in each horizon of the litter-soil system are described by the following set of equations:

$$\frac{dQ_{Cs}^{RES}}{dt} = k_{Cs}^{RES}\left(Q_{Cs}^{sol} - \frac{Q_{Cs}^{RES}}{b_{Cs}^{RES}}\right), \tag{1}$$

$$\frac{dQ_{Cs}^{FES}}{dt} = k_{Cs}^{FES}\left(Q_{Cs}^{sol} - \frac{Q_{Cs}^{FES}}{b_{Cs}^{FES}}\right), \tag{2}$$

where Q_{Cs}^{RES} and Q_{Cs}^{FES} represent ^{137}Cs content on RES and FES, respectively; k_{Cs}^{RES} and k_{Cs}^{FES} are the constants of sorption rates on RES and FES; b_{Cs}^{RES} and b_{Cs}^{FES} are the buffer constants.

The buffer constants are estimated based on the quasi-equilibrium condition between ^{137}Cs content in soil solution and on sorption sites. Since all the cations found in soil solution complete for nonselective sites, the buffer constant of ^{137}Cs sorption on RES can be expressed (using representations of [4]) as

$$b_{Cs}^{RES} = \frac{[RES](\rho / \theta_v)}{\sum_i \dfrac{q_{M_+^i}}{k_s^{RES}(Cs / M_+^i)} + \sum_j \dfrac{\sqrt{q_{M_{2+}^j}}}{k_s^{RES}(Cs / M_{2+}^j)}}, \tag{3}$$

where $[RES]$ is the potential RES capacity; q_{M+} and q_{M2+} are the concentrations of uni- and bivalent cations in soil solution; k_s are the selectivity factors of ^{137}Cs ion exchange in relation to uni- and bivalent cations; ρ is the soil layer density; θ_v is the layer moisture by volume.

The buffer constant of ^{137}Cs sorption on FES, taking into account that only univalent cations complete with ^{137}Cs, is expressed as follows:

$$b_{Cs}^{FES} = \frac{[FES](\rho / \theta_v)}{\sum_i \dfrac{q_{M_+^i}}{k_s^{FES}(Cs / M_+^i)}}. \tag{4}$$

^{137}Cs fixation by clay minerals without regard for collapse effects induced by the use of ameliorants is described by the following formula:

$$\frac{dQ_{Cs}^{fix}}{dt} = k_{Cs}^{fix}\left(Q_{Cs}^{FES} - \frac{Q_{Cs}^{fix}}{b_{Cs}^{fix}}\right), \tag{5}$$

where Q_{Cs}^{fix} is the radionuclide content in the fixed form; k_{Cs}^{fix} and b_{Cs}^{fix} are the fixation and buffer constants, respectively.

It has been assumed that the rate of the collapse process of the wedge-shaped zones and thereby ^{137}Cs fixation in the crystal lattice of clay minerals after the application of K fertilizers depends on the content of extra K amounts in soil solution. An additional ^{137}Cs flux from FES into the fixed form is formulated this way:

$$F_{coll} = k_{coll} \cdot Q_{Cs}^{fix} \cdot \Delta q_K^{sol}, \tag{6}$$

where Δq_K^{sol} is the difference between actual K concentration in soil solution and "natural" k concentration (without fertilizing) typical for the soil type considered.

When modelling consequences of the dolomite powder application it has been assumed that increase in the content of Ca^{2+} ions in soil solution results in the wedge-shaped zone stabilization effect and ^{137}Cs fixation in the crystal lattice of clay minerals with subsequent decrease in Ca^{2+} content in solution ("delayed collapse"). The buffer constant after the application of dolomite powder (b_{Cs}^{FES*}) is described as:

$$b_{Cs}^{FES*} = b_{Cs}^{FES}(1 + k_{Ca1}(1 - \exp(-k_{Ca2}\Delta q_{Ca}))) , \qquad (7)$$

where Δq_{Ca}^{sol} is the difference between Ca concentration in soil solution after the use of ameliorant and "natural" Ca concentration typical for the soil type considered. The flux, which reflects ^{137}Cs transfer to fixed form dependents of the rate of Ca removal from soil solution of the horizon considered:

$$F_{Cs}^{fix} = k_{Cs}^{fix*} \cdot \sum F_{Ca}^i \cdot Q_{Cs}^{FES} , \qquad (8)$$

where ΣF_{Ca}^i - is the sum of fluxes responsible for decrease in the concentration of calcium cations in soil solution of the horizon considered.

When modelling the process of ^{137}Cs uptake by the root system of plants, the rate of this process was assumed to be governed by ^{137}Cs concentration in soil solution – q_{Cs}^{sol} [mM l^{-1}]:

$$q_{Cs}^{soli} = \frac{Q_{Cs}^{soli}}{\lambda N_A \theta_v^i h^i} , \qquad (9)$$

where N_A is the Avogadro number, λ is the radioactive decay constant, θ_v^i is the volumetric moisture of the i-th layer of litter or soil, h^i is the i-th layer depth. In the description of ^{137}Cs uptake by plants from each soil layer, the Michaelis-Menten representation [5] was used modified with the account of K competing effect. In addition an assumption was made that the rate of ^{137}Cs accumulation by plants is proportional to the rate of biomass increases. In this case ^{137}Cs concentration in plants is defined as follows:

$$C_{Cs}^v = C_m \sum_i \frac{\delta_i q_{Cs}^{soli}}{K_m + q_{Cs}^{soli} + a\Delta q_K^{soli}} , \qquad (10)$$

where δ_i – is the proportion of roots in the i-th layer of the litter-soil system; V_m, K_m, α are the constants.

Supposing ^{137}Cs sorption in the root exchange complex obeys general laws of the cation exchange, ^{137}Cs concentration in plants when soil solution is dominated by Ca^{+2} ions can be described as follows:

$$C_{Cs}^v = C_m \sum_i \frac{\delta_i q_{Cs}^{soli}}{K_m + q_{Cs}^{soli} + b\sqrt{\Delta q_{Ca}^{soli}}} . \qquad (11)$$

The developed model was parameterized for soils off the coniferous forest located in the Bryansk region in area suffered from the radioactive fallout after the Chernobyl accident. In parameterization experimental and literature data were used, reported in [4-7]. The verification of the model suggests that it satisfactorily describe ^{137}Cs behaviour in the soil-plant system following the application of ameliorants.

4. SELECTED RESULTS

The described model was employed to study ^{137}Cs behaviour in forest soils in different situations connected with the application of countermeasures. Fig.2 summarized results from the calculations of the dynamics of ^{137}Cs content in components of organo-mineral horizon of semihydromorphic soils after K fertilizing. Lowering of ^{137}Cs content in soil solution after the use of dolomite powder is of a more prolonged character due to slow Ca transfer to ion form after the application of this ameliorant and delayed collapsing of clay minerals layers.

A comparative analysis was carried out of the effects of ^{137}Cs fixation in soil and decrease in the rate of ^{137}Cs root uptake from soil solution on the reduction in TF ^{137}Cs to berries of bilberry growing on semihydromorphic soils in coniferous forest after the use of ameliorants. The reduction in TF ^{137}Cs, resulting from the application of both dolomite powder and K fertilizers was found to be primarily caused by changes in ^{137}Cs bioavailability in soil. The contribution of processes connected with the decline of ^{137}Cs root uptake rate is greater in the event of K fertilizing.

Fig. 3 illustrates the estimated dynamics of ^{137}Cs accumulation in plants with the application of K fertilizers at different times after radioactive fallout. The ratio of TF ^{137}Cs to bilberry (berries) in the absence of countermeasures to that after the use of K fertilizers is practically independent on the year of countermeasure application. At the same time, the value of the absolute TF decrease in case of countermeasures application is lower in the distant than in the early period.
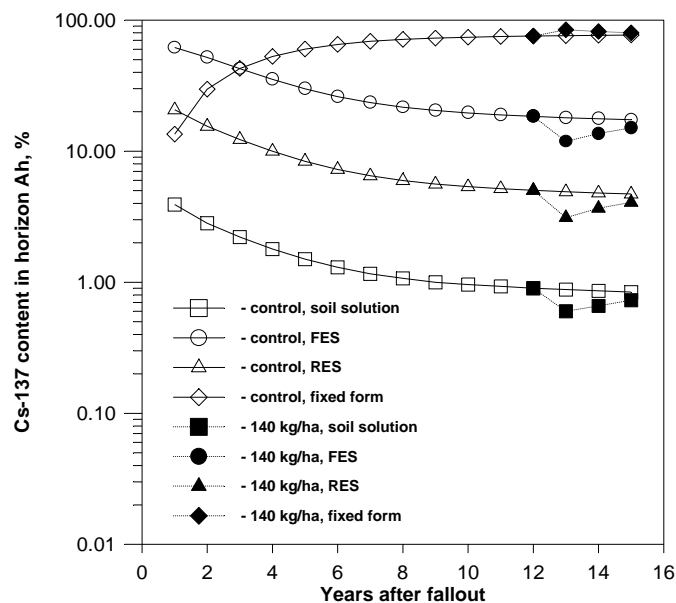

Figure 2. Estimated dynamics of ^{137}Cs content in components of Ah-horizon of semihydromorphic forest soils after K fertilizing and in control.
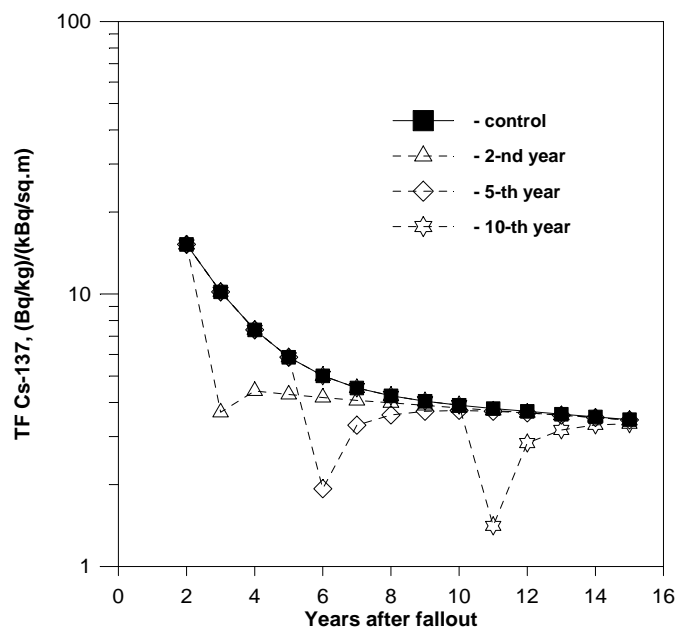

Figure 3. Dynamics of TF ^{137}Cs to berries of bilberry plants in case of K fertilizing 2, 5 and 10 years after radioactive fallout.

The models developed are effective tools to study ^{137}Cs behaviour in the soil-plant system after the application of ameliorants. The suitability of the models use for research purposes is caused by the description of the mechanisms governing physico-chemical processes in soil and responsible for the rate of ^{137}Cs accumulation by plants.

References

[1] Management on the implementation of countermeasures in the agriculture after a nuclear accident. Vienna: IAEA-TEC-DOC-745, 1994.
[2] Cremers A., Elsen A., De Preter P., Maes A., *Nature.* 1988, V. 333, pp. 247-249.
[3] Konoplev A.V., Bulgakov A.A., Popov V.E., et al., Contaminated Forests. Recent Developments in Risk Identification and Future Perspectives. NATO Sci. Ser. 2, Environ. Security, 1999, V. 58, pp. 217-229.
[4] Orlov D.S., Soil chemistry. Moscow, MGU Publishers, 1985, 376 p.
[5] Barber S.A., Biological availability of nutrients in soil. Moscow, Agropromizdat, 1988, 375 p.
[6] Konopleva I.V., Study of ^{137}Cs bioavailability in soils of forest ecosystems. Ph. D thesis. Obninsk, RIARAE, 1999, 27 p.
[7] Yagodin B.A., Smirnov P.M., Peterburgsky A.V., et al., Agrokhimia, Moskow, Agropromizdat, 1985, 655 p.