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THEORY OF THE EFFECT OF INHIBITION OF TRANSFER OF RADIONUCLIDES AND HEAVY METALS FROM SOIL TO PLANTS BY EFFECTIVE AMELIORANTS. III. CALCULATIONS AND EXPERIMENTAL MEASUREMENTS

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Analytical solutions have been obtained for determination of the linear velocity of ions on the surface of plant roots. Relative amounts of a nuclide (or some other ion) that is transferred to plants from the soil are evaluated theoretically and determined experimentally.

In [1] we considered a model (equations) of convective diffusive transfer of nutrient elements from soil to plants. Following this model, it is possible to write

$$\frac{Q_1}{Q_2} = \frac{V_1}{V_2}\left[\frac{2k_1 - V_1}{V_1}\exp\left(\frac{k_1 - V_1}{D_1^*}k_1 t\right)\operatorname{erfc}\left(\frac{2k_1 - V_1}{2}\sqrt{\left(\frac{t}{D_1^*}\right)}\right) + \right.$$

$$\left. + \operatorname{erf}\left(\frac{V_1}{2}\sqrt{\left(\frac{t}{D_1^*}\right)} + 1\right)\Bigg)\right]\left[\frac{2k_2 - V_2}{V_2}\exp\left(\frac{k_2 - V_2}{D_2^*}k_2 t\right)\times\right.$$

$$\left.\times \operatorname{erfc}\left(\frac{2k_2 - V_2}{2}\sqrt{\left(\frac{t}{D_2^*}\right)}\right)\operatorname{erf}\left(\frac{V_2}{2}\sqrt{\left(\frac{t}{D_2^*}\right)} + 1\right)\right]^{-1}, \tag{1}$$

where Q_1 and Q_2 are the amount of the nuclide (or some other element) absorbed by unit length of the root in the time t in the case of an applied ameliorant and in the control, respectively; k_1 and k_2 are the linear velocities of the nuclide absorbed by the surface of the root (absorptive capacity); D_1^* and D_2^* are the ionic diffusion coefficients in the soil; V_1 and V_2 are the linear velocities of the ion displaced in the soil by the action of the flow of moisture to the root.

It should be noted that at $V > k$, i.e., when the rate of nuclide transfer by water is higher than the rate of absorption of the nuclide by the surface, the nuclide accumulates near the root surface, at $k > V$ the amount of the nuclide at the root decreases, and at $V = k$ the nuclide concentration in the soil does not change and remains equal to the initial concentration.

In [1, 2] results of experimental investigations and theoretical calculations of ameliorant-induced changes in the diffusion coefficients of ions in soil were presented, and in this paper an attempt is made to calculate k_1 and k_2 and, eventually, Q_1/Q_2 as well as to determine V_1 and V_2.

Following [3, 4] and other works, it is possible to write

$$V = V_0\frac{\beta}{(1 + \beta)\,n}, \tag{2}$$

where V_0 is the velocity of water on the root surface; β is the ion distribution coefficient in the soil, i.e., the ratio of ion concentrations in the solid phase of the soil and in the soil solution; n is the porosity of the soil.

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According to the results of our experiments [1], for the loamy sandy soil studied $\beta = (1-10)\cdot 10^{-3}$.

It is necessary to estimate the ameliorant-induced changes in β. An experimental method for determination of β was given in [1], but another method can also be used to find this coefficient.

As is shown in [4],

$$\beta^* = \frac{D^*}{D_0^* - D^*}, \tag{3}$$

where D^* is the diffusion coefficient of the sorbed indicator (ion); D_0^* is the diffusion coefficient of the nonsorbed indicator (ion).

In systems with high-rate sorption $D_0^* >> D^*$, and then

$$\beta^* = \frac{D^*}{D_0^*}, \tag{4}$$

Consequently,

$$\frac{\beta_1^*}{\beta_2^*} = \frac{D_1^*}{D_2^*} \tag{5}$$

and

$$\frac{V_1}{V_2} = \frac{D_1^*}{D_2^*}, \tag{6}$$

where β_1^* and β_2^*, D_1^* and D_2^* are the ion distribution and diffusion coefficients in ameliorant-modified and nonmodified soil.

Experimental relations of the type of $D^* = A\beta^*$ (where A is a constant) that confirm formula (5) are given in [5]. In what follows, numerical values of the parameters in formula (2) will be presented (for the systems studied). It should be noted that the velocity of water flowing on the root surface was determined as follows:

$$V_0 = K_p \Delta z, \tag{7}$$

where K_p is the water-permeability coefficient of root sections; Δz is the root pressure.

Now, the rate of ion absorption by the surface of the root will be determined.

The factors that affect the absorbing capacity of a root are discussed in detail in [5]. The ion concentration in the soil, the radius of the root, temperature, the presence of competing ions, availability of oxygen, the effect of other plants, transpiration and water stress, and the flow of nutrients to the plant can be mentioned among these factors.

It is quite evident that some of the factors are independent of the applied ameliorant (for example, the radius of the root, temperature, or the effect of other plants), but changes in the absorbing capacity of the root should be determined by the ameliorant.

With the assumption that the root is an active transmitting membrane that can be treated by the methods of irreversible thermodynamics, in [5] the following relation was given between the flow of dissolved compounds F and the water velocity V_0 through the root surface, which agrees well with the available experimental data:

$$F = (1 - S)\, C_{ea} V_0 \tag{8}$$

where S is the selectivity coefficient; C_{ea} is the ion concentration on the root surface.

TABLE 1. Rates of Potassium Absorption by the Root System of Barley

Absorption by unit volume of root system S_r, g-eq/g·sec·10^{-10}	Linear velocity of nuclide on root surface $k \cdot 10^{-4}$, cm/sec
0.34	0.12
2.10	0.037
5.60	0.18

In [3] a different approach to determination of the velocity of ions through the membrane is given for the case of low concentrations. This is expressed analytically in the following way:

$$k = \frac{D_{sm} \beta_{sm}}{\delta}, \tag{9}$$

where D_{sm} is the effective diffusion coefficient in the membrane; β_{sm} is the ion distribution coefficient between the membrane and the environment; δ is the thickness of the membrane.

In [6, 7] formula (9) is given in the form

$$k = \frac{D_{sm}}{\delta} \mathrm{Pe}. \tag{10}$$

where Pe is the Peclet number.

It should be noted that use of formulas (8)-(10) is difficult because of the complicated determination of D_{sm}, β_{sm}, and Pe inside the root system.

Interesting results were obtained from analysis of k for potassium absorbed by the root system of barley (see Table 1, taken from [5]). The quantity S_r in the table is determined from the well-known formula

$$S_r = \frac{2kC_{ea}}{a_r}, \tag{11}$$

where C_{ea} is the ion concentration on the surface; a_r is the radius of the root. It is quite clear that the absorption rate of the potassium ion should increase with S_r, but as one can see from Table 1, this not the case. Consequently, measuring the velocity of the ion on the surface of the root will require a rigorous and very complicated procedure.

The following method can be proposed for solution of this problem. Assuming that the dimensions of the pores of the surface of a root hair are commensurable with the atomic and molecular dimensions of a moving particle, and using the Einstein–Stokes relation, we can write

$$\frac{D_0}{D_1} = \frac{f_1}{f_0}, \tag{12}$$

$$\frac{D_0}{D_2} = \frac{f_2}{f_0}, \tag{13}$$

where D_0 is the diffusion coefficient of water molecules in the root (membrane); D_1, D_2 are the ion diffusion coefficients in the root (membrane) in the ameliorant-modified soil and in the control; f_0 is the friction coefficient due to motion of water along the pore (channel) inside a root hair; f_1 and f_2 are the friction coefficients due to motion of a cluster ion, surrounded by water molecules in a root hair, in the soil with and without application of the ameliorant.

Equations (12) and (13) can be written as follows:

$$\frac{V_0}{k_1}\beta_{1m} = \frac{f_1}{f_0}, \tag{14}$$

$$\frac{V_0}{k_2}\beta_{2m} = \frac{f_1}{f_0}, \tag{15}$$

where β_{1m} and β_{2m} are the ion distribution coefficients in the pore space of the root in the soil with and without application of ameliorant. Then,

$$k_1 = V_0\beta_{1m}\frac{f_0}{f_1}, \tag{16}$$

$$k_2 = k_1\frac{f_1}{f_2}\,\frac{\beta_{1m}}{\beta_{2m}} \tag{17}$$

or

$$k_2 = k_1\frac{D_2}{D_1}\,\frac{\beta_{2m}}{\beta_{1m}}. \tag{18}$$

According to [8], it can be written that

$$D_1\eta_1 = D_1'\eta_1', \tag{19}$$

$$D_2\eta_2 = D_2'\eta_2', \tag{20}$$

$$D_1 = \frac{D_1'\eta_1'}{\eta_1}, \tag{21}$$

$$D_2 = \frac{D_2'\eta_2'}{\eta_2}, \tag{22}$$

where η_1 and η_2 are the viscosity of water inside the root; η_1' and η_2' are the viscosity of water in the bulk of the soil pores; D_1' and D_2' are the ion diffusion coefficients in the soil solution (as before, here subscripts 1 and 2 refer to the ameliorant-modified soil and the control, respectively).

In [5] an analytical relation for determination of D_1' and D_2' is given in the following form:

$$D_1' = \frac{D_1^*}{\theta_1\beta_1 f_{k(1)}}, \tag{23}$$

$$D_2' = \frac{D_2^*}{\theta_2\beta_2 f_{k(2)}}, \tag{24}$$

where θ_1 and θ_2 are the volume moisture content of the soil; $f_{k(1)}$ and $f_{k(2)}$ are the diffusion resistance factor.

Substituting (23) and (24) in (21) and (22), respectively, we obtain

$$D_1 = \frac{D_1^*\eta_1'}{\theta_1\beta_1 f_{k(1)}\eta_1}, \tag{25}$$

$$D_2 = \frac{D_2^* \eta_2'}{\theta_2 \beta_2 f_{k(2)} \eta_2} . \tag{26}$$

Consequently,

$$k_2 = k_1 = \frac{D_2^*}{D_1^*} \frac{\theta_1}{\theta_2} \frac{f_{k(1)}}{f_{k(2)}} \frac{\beta_2}{\beta_1} \frac{\beta_{2m}}{\beta_{1m}} \frac{\eta_1 \eta_2'}{\eta_2 \eta_1'} . \tag{27}$$

It can be easily shown that $\eta_1 \eta_2' / \eta_2 \eta_1' \simeq 1$, and using Eq. (5), we obtain

$$k_2 = k_1 \left(\frac{D_2^*}{D_1^*} \right)^4 \left(\frac{\theta_1}{\theta_2} \right)^2 \left(\frac{f_{k(1)}}{f_{k(2)}} \right)^2 . \tag{28}$$

Proceeding from results presented in [9], we can write

$$\theta_1 = \varepsilon - \varepsilon_{0(1)} ; \quad \theta_2 = \varepsilon - \varepsilon_{0(2)} , \tag{29}$$

where ε is the coefficient of soil porosity; $\varepsilon_{0(1)}$ and $\varepsilon_{0(2)}$ are the coefficients of porosity for a permeability coefficient tending to zero.

Now, we will consider the parameter f_k. As has been found in [5], it accounts for the sinuous trajectory of motion of dissolved compounds through pores and reflects the effect of increase in the diffusion path length, on the one hand, and decrease in the concentration gradient along this path length, on the other. In [5] an analytical relation is also presented:

$$f_k = \theta^{0.5} , \tag{30}$$

which exhibits agreement with experimental values.

Consequently, the final result is

$$k_2 = k_1 \left(\frac{D_2^*}{D_1^*} \right)^4 \left(\frac{\varepsilon - \varepsilon_{0(1)}}{\varepsilon - \varepsilon_{0(2)}} \right)^3 . \tag{31}$$

Now, for determination of k_1 use will be made of the notions and calculated formulas for the friction coefficient due to motion of particles in a liquid given in [10].

According to [10], it is possible to write

$$f = f_h + f_s , \tag{32}$$

where f_h and f_s are the "hard" and "soft" components of the friction coefficient, respectively.

For the "hard" component of the friction coefficient Rise and Allnatt obtained the following formula (also presented in [10]):

$$f_h = \frac{3}{8} \rho G^2 g_{(2)} (G) (\pi m K T)^{1/2} , \tag{33}$$

where ρ is the number density of particles per unit volume; G is the particle diameter; $g_2(G)$ is the radial distribution function at $r = G$; m is the particle mass. At $T >> 293$ K $f_h >> f_s$, and then it is possible to write

$$\frac{f_0}{f_1} = \frac{\rho_0 G_0^2 g_{(2)} (G_0)}{\rho_1 G_1^2 g_{(2)} (G_1)} \sqrt{\left(\frac{m_0}{m_1} \right)} . \tag{34}$$

TABLE 2. Values of Hydrated Radii of Ions (r_1, r_2), Rates of Ion Absorption k_1 by Root Surface at a Water Absorption Rate $V_0 = 1.5 \cdot 10^{-6}$ cm/sec (legumes), Ion Absorption Rates k_2 at $V_0 = 1.5 \cdot 10^{-6}$ cm/sec (for loamy sandy soil), and Calculated and Experimental Changes in the Ion Contents Q_1/Q_2 in the Green Material of Peas Grown in Loamy Sandy Soil

Ion	Hydrated radii, Å		Ion absorption rates × 10^8, cm/sec		Q_1/Q_2	
	r_1	r_2	k_1	k_2	calculated	experimental
Cs^+	1.963	4.101	0.86	5.50	0.22	0.22
Sr^{2+}	2.950	5.143	2.51	16.06	0.24	–
Cd^{2+}	4.282	6.466	11.57	74.03	0.67	0.5
Pb^{2+}	5.444	8.430	11.98	28.36	0.88	0.90
K^+	5.651	7.614	14.85	10.91	1.30	1.12

Formula (34) will be used in subsequent calculations. But for determination of f_0/f_r it is necessary to evaluate radii of hydrated ions.

According to [11, 12] and some other works, the potential E_c (potential energy) of the ion-dipole interaction in a medium with a dielectric constant ε_0' is determined as follows:

$$E_c = -\frac{ze\bar{m}}{\varepsilon_0' \varepsilon_0'' r_1^2}, \tag{35}$$

and in vacuum

$$E_c = -\frac{ze\bar{m}}{\varepsilon_0'' r_1^2}. \tag{36}$$

Then

$$\Delta E_c = \frac{ze\bar{m}}{\varepsilon_0'' r_1^2}\left(1 - \frac{1}{\varepsilon_0'}\right), \tag{37}$$

where ΔE_c is the change in the potential energy; z is the charge (valence) of the ion; m is the dipole moment of a water molecule; ε_0'' is the electric constant, equal to $8.85 \cdot 10^{-12}$ F/m; r_1 is the distance from the center of the ion to the center of the dipole (the hydrated radius of the ion); e is the charge of the electron.

Equivalently,

$$r_1 = \sqrt{\left(\frac{ze\bar{m}}{\varepsilon_0'' \Delta E_c}\left(1 - \frac{1}{\varepsilon_0'}\right)\right)}. \tag{38}$$

In formula (38) all the parameters except ΔE_c are known. For determination of ΔE_c use was made of NMR spectroscopy in the following way. The relative relaxation times of water molecules were found in NMR spectra obtained for solutions of different salts at different concentrations. The method used for calculation of ΔE_c is described in our work [13], and calculated values of r_1 and r_2(r_2 is the distance from the center of the cation to the oxygen atom in the H_2O molecule completing formation of the dimer) are given in Table 2.

We continue simplification (particularization) of formula (34). To do this, we determine the parameters characterizing the friction coefficient caused by motion of the water molecule in the pore space of the membrane (the root system).

With a tetrahedral environment of the central molecule H_2O

$$\rho_0 = \frac{1}{V_m} = \frac{9}{8}\,\frac{\sqrt{3}}{R_0^3}, \tag{39}$$

where V_m is the volume per molecule; R_0 is the distance between the adjacent oxygen atoms in liquid water.

The radial distribution function $g_{(2)}(G_0)$ is considered to be a factor [14] whose value indicates the difference between the local density $\rho(\overline{R})$ at the distance $\overline{R}$ and the bulk density of the liquid. At long distances from the central molecule $g_{(2)}(R)$ is unity. However, in the neighborhood of the central molecule the local density, differs from the bulk density and its maximum value $g_{(2)}(G_0)$ is equal to

$$g_{(2)}(G_0) = \frac{m_0}{V_m} = \frac{M_0}{N_A}\,\frac{9\sqrt{3}}{8\,R_0^3}, \tag{40}$$

where M_0 is the molecular weight of water; m_0 is the mass of a water molecule; N_A is Avogardo's number.

For determination of the parameters that characterize the friction coefficient of the ion moving in the pore space of the membrane (root), we consider the ion as a particle with a cation placed at its center, surrounded by eight dimers of water molecules located at the vertices of a cube. Then, the side of the cube is

$$a_1 = \frac{2}{\sqrt{3}}\,r_2$$

and consequently,

$$\rho_1 = \frac{N_1 3\sqrt{3}}{8 r_2^3}, \tag{41}$$

where $N_1 = 17$ is the number of particles in the cluster (cube).

The radial distribution function $g_{(2)}(G)$ is found as follows:

$$g_{(2)}(G) = \frac{3\sqrt{3}}{8}\,\frac{M_1 + M_0(N_1 - 1)}{r_2^3 N_A}, \tag{42}$$

where M_1 is the atomic weight of the ion. Then,

$$k_1 = \frac{9}{4}\,\frac{V_0 r_2^4 M_0^{3/2} \beta_{1m}}{N_1 R_0^4\,[M_1 + M_0(N_1 - 1)]^{3/2}}. \tag{43}$$

In formula (43) the parameter β_{1m} is unknown. The following conditions will be adopted for its estimation:

1. It should be remembered that all calculations for determination of D_1, D_2, D_1^*/D_2^*, β_1, β_2, β_1/β_2 [2] refer to systems in which the concentration of migrating ions is relatively small (at $c \to 0$).

2.

$$\beta_{1m} < \beta_{2m} \quad \text{and} \quad \frac{\beta_{2m}}{\beta_{1m}} = \left(\frac{D_1^*}{D_2^*}\right)^2 \left(\frac{\varepsilon - \varepsilon_{0(1)}}{\varepsilon - \varepsilon_{0(2)}}\right)^{3/2}.$$

3. Application of the ameliorant increases the active porosity of the soil $(\varepsilon - \varepsilon_0)$ and decreases the concentration of migrating ions in the roots. This means that the ion diffusion coefficient and the ion distribution coefficient decrease in the pore space of the root.

4. Assuming that the dimensions of the pores of the surface of a root hair are commensurable with atomic or molecular dimensions, it can be concluded that the minimum value $\beta_{1m} = 1$, i.e., upon entering a pore space the hydrated ion occupies its entire volume.

5. As the concentration of migrating ions in the soil increases, so do the diffusion coefficient and the distribution coefficient inside the pore space of the root. This condition characterizes the state of the soil without an ameliorant.

Therefore, in our calculations, for determination of k_1, $\beta_{1m} = 1$ is assumed.

In Table 2 values of k_1 are given that were obtained for an average rate of water absorption by the surface of legume roots of $1.5 \cdot 10^{-6}$ cm/sec (according to [15]).

Now, we present calculated results (for comparison with experimental measurements) for the change in the content of cesium-157, strontium-90, cadmium, lead, and potassium (which appears in soil upon application of the ameliorant) in the green material of peas grown in a pilot plot of the Karl Marx Collective Farm, Loev district, Gomel region. The soils of the plot are loamy sand, the radiocontamination level is 20 Ci/km^2; quick lime and phosphogypsum were used as ameliorant, which were applied at a dose of 5 ton/ha each.

As follows from formula (31), for determination of k_2 it is necessary to know the following: the coefficient of porosity ε at complete water saturation; the coefficients of porosity $\varepsilon_{0(1)}$ and $\varepsilon_{0(2)}$ corresponding to the state of the ameliorant-modified and intact soils at a permeability coefficient close to zero; the relative ion diffusion coefficient D_1^*/D_2^* in the soil corresponding to the actual concentration of the filtering solution. According to measurement, $\varepsilon = 0.943$, $\varepsilon_{0(1)} = 0.430$, $\varepsilon_{0(2)} = 0.558$. In the case of migration of cesium-137, strontium-90, cadmium, and lead: $D_1^* = 6.09 \cdot 10^{-8}$ cm^2/sec, $D_2^* = 7.94 \cdot 10^{-8}$ cm^2/sec, $V_1 = 0.48 \cdot 10^{-8}$ cm/sec, $V_2 = 0.35 \cdot 10^{-8}$ cm/sec.

Calculated values of k_2 are presented in Table 2.

By substituting the values of k_1 and k_2, D_1^* and D_2^*, V_1 and V_2 for $t = 5 \cdot 10^6$ sec into Eq. (1), we determined changes in the amount of ions Q_1/Q_2 transferred from the soil to the roots (Table 2).

As follows from Table 2, the calculated and experimental Q_1/Q_2 are similar. Thus, application of quick lime and phosphogypsum ensures a rapid decrease in the amount of radioactive cesium and strontium in the agricultural products. For heavy soils this effect is much more pronounced.

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