Atomic Energy, Vol. 88, No. 2, 2000

^{90}Sr AND ^{137}Cs EXCHANGE DISTRIBUTION COEFFICIENT IN SOIL-WATER SYSTEMS

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UDC 504.45.054:621.039.586

Two methods are proposed for estimating the exchange distribution coefficient of ^{137}Cs and ^{90}Sr in natural soil-water systems: effective selectivity and selective sorption of ^{137}Cs. Principles for classifying soils and deposits as a function of the effective selectivity coefficient are proposed. Using the first method, the ^{90}Sr distribution coefficient can be estimated if the sorption properties of the medium are known to within 50%: for ^{137}Cs, the distribution coefficient can be estimated only in order of magnitude. The uncertainty in the prediction of the ^{137}Cs distribution can be decreased by determining the characteristics of the selective sorption of ^{137}Cs: the capacity of selective sorption centers and/or the radiocesium interception potential. 3 tables, 8 references.

The present work is a continuation of the investigations in [1] and is devoted to the development and analysis of methods for estimating the exchange distribution coefficient as a step in the prediction of ^{90}Sr and ^{137}Cs distributions in soil-water systems.

Effective Selectivity Method. Since ^{90}Sr and ^{137}Cs in solution are primarily in the form of cations, their exchange sorption occurs by the cationic exchange mechanism. The sorption-desorption equilibrium of the cation of a radionuclide R with the cation M with the same charge is characterized by the selectivity coefficient

$$K_c(R/M)=\frac{[R]_{ex}[M]_w}{[R]_w[M]_{ex}},$$

where $[R]_{ex}$ and $[M]_{ex}$ are the content of the exchange forms of the radionuclide and the competing cation in the solid phase and $[R]_w$ and $[M]_w$ are their concentration in an aqueous extract.

The selectivity coefficient can be measured by the method of successive extractions, in which the concentration of the radionuclide and competing ions are determined in the aqueous extract and the content of the exchange form of the radionuclide and competing ions in the solid material are determined in the salt extract. The dimensionless selectivity coefficient is related with the distribution coefficient K_d^{ex} (liters/kg) of the exchange form of the radionuclide as follows:

$$K_d^{ex}(R)=K_c(R/M)([M]_{ex}/[M]_w)=K_c(R/M)K_d^{ex}(M). \tag{1}$$

This equation is valid for any competing ion. At the same time, for most soils and bottom deposits Ca^{2+} is the determining exchange ion in the case of ^{90}Sr. For ^{137}Cs, depending on the conditions, either K^+ or NH_4^+ ammonia predominates under reducing conditions in bottom deposits and peat-bog and organic forest soils. Nonetheless, K^+ can be used as an analog for cesium. The effective selectivity coefficient $K_c^{eff}(R/M)$, determined in this manner, for a radionuclide with respect to the cation analog serves as a basis for predicting the exchange distribution coefficient.

The advantage of this method lies in the fact that standard procedures are used to determine the parameters. In addition, many required data can be found in the literature; this is especially important when the consequences of an accident must be predicted quickly.

Scientific and Industrial Association Taifun. Translated from Atomnaya Énergiya, Vol. 88, No. 2, pp. 152–158, February, 2000. Original article submitted June 11, 1999.

1063-4258/00/8802-0158$25.00

TABLE 1. Effective Exchange Selectivity Coefficient for Strontium and Calcium Cations in Soil Suspensions and Individual Components of Soil

Solid phase	Amount of adsorbed strontium, % of cationic exchange capacity	K_c^{eff}	Reference
	Soils		
Organic soil with humus content, %			
50	~50	0.6–0.7	[2]
21	Traces – 3.1	1	[3]
87	Traces – 0.5	0.8	[3]
21–89	Traces	1.7 ± 0.2	[3]
12 soils with different humus content	Traces – 7.5	1.1 ± 0.3	[4]
	Soil components		
Bentonite	1	1.8	[2]
	7	1.2	[2]
Vermiculite	0.5	1.3	[2]
	7	1.1	[2]
Monmorillonite	~50	1.3	[5]
Illite	~50	1.0	[5]
Caolinite	~50	1.0	[5]
Vermiculite	~50	1.4	[5]
	Traces	1–1.2	[2]
	~50	0.65	[2]
Humic acids	$5 \cdot 10^{-3} - 5$	0.69	[2]
	$5 \cdot 10^{-3} - 5$	0.66	[3]
	Traces – 1.4	0.69	[3]
	Traces – 1.3	0.66	[3]

For ^{90}Sr, which is sorbed nonselectively by soil, the exchange selectivity coefficient of strontium and calcium ions K_c^{eff}(Sr/Ca) varies from 1 to 2 in most cases. The distribution coefficient for ^{90}Sr can be determined from Eq. (1) to within 50%. Humic acids and organic soil adsorb calcium cations somewhat better, though there are exceptions to this rule (Table 1). Conversely, minerals predominantly adsorb strontium cations. There is also a tendency for the effective exchange selectivity coefficient of strontium and calcium cations to decrease as the quantity of adsorbed strontium increases, but in all cases this coefficient differs from 1 by less than a factor of 2.

According to measurements performed for soil in Bryansk Oblast and the 30-km zone around the Chernobyl nuclear power plant, the average effective exchange selectivity coefficient for strontium and calcium cations is 1.2 ± 0.4 (Table 2), which agrees with the data in Table 1 and also with [6].

The effective exchange selectivity coefficient for the cesium-potassium cation pair, in contrast to strontium-calcium, in the first place, is much greater than 1 for most soils and deposits and, in the second place, varies over a much wider range (according to our data, from 2 to 200). This is due to the substantial differences in the affinity of soil sorption centers to the cesium cation.

The entire diversity of ion-exchange sorption centers was divided, on the basis of a study of the sorption of the cesium ion by illite, into three basic types with substantially different selectivity [4]. Sorption locations with maximum capacity and minimum selectivity with respect to cesium were classified as ordinary surface ion-exchange centers. The two other types of sorption locations with a lower capacity but much higher selectivity are called V-type, since they are located in regions where the edge parts of the interstack spaces of the crystal lattice of illite-type minerals expand toward the surface. In the English literature, nonselective sorption centers located on the surface of particles are labeled as RES (regular exchange sites), and sorp-

TABLE 2. Effective Exchange Selectivity Coefficient for Strontium and Calcium Cations in Soil Suspensions from the 30-km Zone Around the Chernobyl Nuclear Power Plant and Bryansk Oblast

Soils (number of samples)	Sampling location	Layer, cm	K_c^{eff}
Soddy-podzolic long-cultivated light-textured loam (2)	Chernobyl	0–0.5	1.0 ± 0.1
		1–2	1.1 ± 0.1
		2–4	1.6 ± 0.2
		4–6	1.8 ± 0.1
		6–10	1.5 ± 0.4
Alluvial soddy acidic sandy loam:	Left-bank flood plain of the Pripyat' River		
site 1 (2)		0–2	1.7 ± 0.4
		2–4	1.7 ± 0.3
site 2 (2)		0–5	1.0 ± 0.1
		5–10	1.0 ± 0.3
Soddy podzolic long-cultivated sandy loam (2)	Village of Korogod	0–0.5	1.1 ± 0.1
		0–1	1.2 ± 0.4
		1–2	1.0 ± 0.1
Alluvial soddy acidic light-textured loam (1)	Village of Rudnya Il'inetskaya	0–0.5	0.6
Soddy-average podzolic light-textured loam (1)	Village of Kliviny	0–0.5	0.7
		0–5	0.9 ± 0.3
		5–11	0.8 ± 0.2
Peat-bog (2)	Bryansk Oblast	11–17	0.9 ± 0.1
		17–22	0.7 ± 0.1
		22–27	1.0 ± 0.1
		0–2	1.6 ± 0.1
Soddy-podzolic gleyey (2)	Same	2–4	1.9 ± 0.4
		4–6	1.8 ± 0.6
		8–10	1.4 ± 0.3
Soddy-podzolic long-cultivated sandy loam (1)	Same	0–2	1.9

tion centers located between layers of the crystal lattice in the region of their expanded edges are labeled as FES (frayed edge sites) [7].

The specific arrangement of V-type sorption centers is due to their high selectivity with respect to ions with a low hydration energy. The diameter of cations in a hydrated state is larger than the size of the V-type edges of interstack spaces. However, ions with a low hydration energy, such as K^+, Rb^+, NH_4^+, and especially Cs^+, can easily lose hydration water, penetrate into the expanded edge regions of interstack spaces of minerals, and be sorbed on the excess negative charges located there. At the same time, ions with a relatively high hydration energy (Ca^{2+}, Mg^{2+}, Sr^{2+}), surrounded by a large hydration shell, cannot penetrate to V-type centers and are sorbed exclusively on particle surfaces. ^{137}Cs sorbs nonselectively on surface centers, i.e., its sorption selectivity coefficient with respect to other singly charged ions (K^+, Na^+, NH_4^+) is close to 1. At the same time, the sorption selectivity coefficient of cesium on V-type centers is 1000 with respect to K^+ and 200 with respect to NH_4^+ [5]. Selective sorption centers comprise a relatively small fraction of the total number of ion-exchange sorption locations: from 1 to 5% for most soils and bottom deposits [5, 7].

As a result of the high selectivity of V-type sorption centers with respect to cesium and the fact that ^{137}Cs and even stable cesium are found in the surrounding medium in trace quantities, almost all ^{137}Cs is sorbed selectively in most soils and bot-

TABLE 3. Effective Exchange Selectivity Coefficient for Cesium and Potassium Cations in Soil Suspensions from the 30-km Zone of the Chernobyl Nuclear Power Plant and Bryansk Oblast

Soils (number of samples)	Sampling location	Layer, cm	K_c^{eff}
Soils with organic matter content less than 20%			
Alluvial soddy acidic light-textured loam (4)	Village of Rudnya Il'inetskaya	0–0.5	7 ± 4
Soddy-podzolic sandy loam (2)	Village of Staraya Rudnya	0–0.5	14.6 ± 0.4
Soddy alluvial light-textured loam (2)	Village of Benevka	0–0.5	17 ± 7
Soddy-average podzolic light-textured loam (2)	Village of Kliviny	0–0.5	5.0 ± 0.5
Soddy-podzolic long-cultivated sandy loam (2)	Village of Korogod	0–0.5	8 ± 3
Surface-podzolic sandy loam (2)	Village of Kopachi	0–0.5	13 ± 3
Soddy-podzolic long-cultivated light-textured loam (3)	Chernobyl	0–0.5	6 ± 4
		0–1	9 ± 3
Alluvial soddy acidic sandy loam:	Left-bank flood plain of the Pripyat' River		
site 1		0–5	7 ± 2
site 2		0–5	8 ± 2
Soddy-podzolic long-cultivated sandy loam (1)	Bryansk Oblast	0–2	12
Soddy-slightly podzolic sandy loam (3)	Same	0–4	13 ± 2
Soddy long-cultivated sandy loam (1)	Same	0–2	11
40–60%			
Peat-bog (2)	Bryansk Oblast	0–5	4.6 ± 0.8
		5–11	4 ± 2
		11–17	3 ± 2
		17–22	6 ± 4
Soddy-podzolic gleyey light-textured loam (1)	Same	0–1	3.1
		1–2	3.5
		2–4	3.8
		4–6	3.9
		6–8	3.5
		8–10	4.2
Greater than 90%			
Peat-bog (1)	Lake Devok, Great Britain	0–4	1.1
		4–8	1.6
		8–12	1.2
		12–16	0.9
		16–20	1.9
Peat-bog (2)	Same	0–4	1.6 ± 0.6

tom deposits. In most soils, potassium is bound on selective and nonselective sorption centers. A change in the fraction of selectively sorbed potassium leads to a corresponding change in the effective selectivity coefficient. This can occur, for example, when the composition of the pore solution changes. Consequently, strictly speaking, the effective selectivity coefficient is not constant even for the same soil. Nonetheless, the variability of the effective exchange selectivity coefficient for cesium-potassium in natural soil-water systems does not exceed an order of magnitude. Moreover, it can be decreased substantially by introducing differentiated values of the selectivity coefficient for soil with a different content of organic matter, since it is known that the effective exchange selectivity coefficient for cesium-potassium in organic soil is, as a rule, less than in mineral soil.

The average effective exchange selectivity coefficient for cesium-potassium is 9 ± 4 in mineral soil, 4 ± 2 for soils with organic matter content from 40 to 60%, and 1.4 ± 0.5 for 90% (Table 3), i.e., nonselective adsorption of cesium predominates in soil consisting only of organic matter. Thus, an effective exchange selectivity coefficient for cesium-potassium of 9 ± 4 can be recommended for predicting the ^{137}Cs distribution in mineral soil, the value 4 ± 2 is recommended for soil with a humus content of about 50% and 1.4 ± 0.5 for soil consisting predominantly of organic matter.

The average effective exchange selectivity coefficient for strontium-calcium is 1.2 ± 0.3 in mineral bottom deposits in fresh water rivers and lakes and 0.9 ± 0.4 in bottom deposits with organic matter content of about 50%, and for cesium-potassium the exchange coefficient is 8 ± 4 and 6 ± 2, respectively, in mineral and organic deposits. In the general case, to estimate the exchange distribution coefficient, the effective exchange selectivity coefficient can be taken as 1 for the pair strontium-calcium and 7 for cesium-potassium.

Method Based on the Use of the Characteristics of Selective Sorption of Cesium. Another method for estimating the distribution coefficient for ^{137}Cs is based on determining the characteristics of selective sorption. Using the equation for ion-exchange equilibrium for cesium sorption on V-type sorption centers in the presence of a competing ion M^+, it is easy to obtain an expression relating the exchange distribution coefficient for ^{137}Cs with the capacity of Ve-type centers ([FES], mg-equiv/kg) and the M^+ concentration in the solution:

$$K_d^{\mathrm{ex}} = \frac{K_c^{\mathrm{FES}}(\mathrm{Cs}/M)[\mathrm{FES}]}{[M^+]}, \tag{2}$$

where $K_c^{\mathrm{FES}}(\mathrm{Cs}/M)$ is the selectivity coefficient for ion exchange of Cs^+ on V-type sorption centers with respect to the ion M^+.

Rearranging the expression (2), we obtain

$$K_d^{\mathrm{ex}}[M^+] = K_c^{\mathrm{FES}}(\mathrm{Cs}/M)[\mathrm{FES}] = \mathrm{RIP}^{\mathrm{ex}}(M).$$

The expression (2) is a definition of another widely used parameter for selective absorption of ^{137}Cs: the exchange binding potential $\mathrm{RIP}^{\mathrm{ex}}(M)$ (radio cesium interception potential) [3, 7, 8]. The exchange binding potential of cesium is a constant for a given sorbent and characterizes its capacity for selectively and reversibly sorbing cesium.

In the general case, a separate analysis of sorption on selective and nonselective centers can be used to predict the ^{137}Cs distribution coefficient:

$$K_d^{\mathrm{ex}} = K_d^{\mathrm{ex}}(\mathrm{FES}) + K_d^{\mathrm{ex}}(\mathrm{RES}) = \frac{K_c^{\mathrm{FES}}(\mathrm{Cs}/\mathrm{K})[\mathrm{FES}]Z_M}{[\mathrm{K}]_\mathrm{w}} + \frac{K_c^{\mathrm{RES}}(\mathrm{Cs}/\mathrm{K})[M]_{\mathrm{RES}}}{[\mathrm{K}]_\mathrm{w}}, \tag{3}$$

where Z_M is the fraction of V-type sorption centers occupied by M^+ cations; $[M]_{\mathrm{RES}}$ is the concentration of the cation M^+ bound on nonselective sorption centers; $K_d^{\mathrm{ex}}(\mathrm{FES})$ and $K_d^{\mathrm{ex}}(\mathrm{RES})$ are the distribution coefficients of cesium on selective and nonselective sorption centers, respectively.

For nonselective sorption locations, $K_c^{\mathrm{FES}}(\mathrm{Cs}/M)$ is close to 1. In addition, the second term on the right-hand side of the expression (3) is, as a rule, negligibly small compared with the first term for most soils and bottom deposits. On this basis, for the cases where potassium is the dominant ion competing with ^{137}Cs, we have

$$K_d^{\mathrm{ex}}(\mathrm{Cs}) = \frac{\mathrm{RIP}^{\mathrm{ex}}(\mathrm{K})}{[\mathrm{K}]_\mathrm{w}}.$$

In cases where the ammonium is present in substantial quantities in the system,

$$K_d^{\mathrm{ex}}(\mathrm{Cs}) = \frac{\mathrm{RIP}^{\mathrm{ex}}(\mathrm{NH_4})}{[\mathrm{NH_4}]_\mathrm{w}}.$$

In mixed cases, where potassium and ammonium make the same contributions in competition with ^{137}Cs, the following relations can be used:

$$K_d^{\mathrm{ex}}(\mathrm{Cs}) = \frac{\mathrm{RIP}^{\mathrm{ex}}(\mathrm{K})}{[\mathrm{K}]_\mathrm{w} + K_\mathrm{c}^{\mathrm{FES}}(\mathrm{NH_4/K})[\mathrm{NH_4}]_\mathrm{w}};$$

$$K_\mathrm{c}^{\mathrm{FES}}(\mathrm{NH_4/K}) = \frac{\mathrm{RIP}^{\mathrm{ex}}(\mathrm{K})}{\mathrm{RIP}^{\mathrm{ex}}(\mathrm{NH_4})}.$$

This method makes it possible to decrease substantially the uncertainty in estimates of the exchange distribution coefficient, but it is complicated and inaccessible for most territories. At the same time, for critical regions it is recommended that these characteristics be measured in order to increase the reliability of predictions in accidents.

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