

PRIMARY INTERACTION OF RADIOCAESIUM WITH SOIL COMPONENTS AT AERIAL FALLOUT

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Abstract: the initial concentration of ^{137}Cs on the surface of soil aggregates has been confirmed by direct and indirect experiments. The thickness of the surface adsorbing layer has been approximately evaluated. The general pattern of ^{137}Cs distribution on soil aggregates in the A1 horizon of soddy-podzolic heavy loamy undisturbed soil has been obtained using the autoradiography method. The possible effects of the formation of initial gradients of ^{137}Cs concentration in the soil are discussed.

Key words: soil aggregates, autoradiography method, radiocaesium, concentration coefficient, soddy-podzolic soil, interaggregate space, initial gradients of concentration.

The study of distribution of toxicants in the soil profile is one of the traditional problems in their investigation. This problem concerns both experimental and theoretical investigations, including the elaboration of models of substance migration in soil.

However, as the upper soil horizons are aggregated, a toxicant should concentrate first on the surface of aggregates of various sizes due to the soil moisture migration in the interaggregate space and initial sorption interaction with the aggregate surface. The effects of the initial concentration of substances on the surface of aggregates and the approaches to their investigation have been discussed earlier [1, 2, 3].

In addition, if toxicants (in particular, radionuclides) enter the soil in the active vegetation period, plants would play a significant role in the initial consumption of pollutants that are found in significant quantities in surface litter and root residues [4]. Roots are partially located in the interaggregate space, which also influences the initial distribution of toxicants at the aggregate level.

Toxicants are spatially redistributed in a soil aggregate with time to compensate for the initial concentration gradients. Various processes may play the decisive role in this redistribution: (a) the toxicant diffusion inside soil aggregates; (b) the destruction of old aggregates and the formation of new aggregates under the impact of natural and anthropogenic factors, which is equivalent to the mechanical mixing of soil; and (c) toxicant migration from the decomposing plant residue to the mineral part of the soil. The latter mechanism should be most pronounced upon high sorption affinity of a toxicant to the soil.

At present, the dynamics and mechanisms of toxicant redistribution at the aggregate level, as well as the role of soil aggregates in the initial toxicant distribution, are insufficiently studied, which is mainly explained by methodological difficulties.

In this study, we consider the specificity of the initial distribution of ^{137}Cs - a hazardous toxicant - on the surface of soil aggregates. The choice of ^{137}Cs for this study is connected not only with its hazardous effects but also with sufficiently good knowledge on sorption interaction of this radionuclide with soil and its availability to plants through uptake by roots and leaves. It is known that the availability of ^{137}Cs changes with time, which attests to structural changes in the soil - radionuclide interaction. In addition, the results obtained for ^{137}Cs may be extrapolated with certain restrictions on the behavior of a number of other toxicants, radionuclides, and heavy metals.

Objects and research methods

In this article, we present the results of laboratory model experiments performed with a soddy-podzolic heavy loamy soil developed from the mantle loam. The undisturbed soil was sampled from a 10-year-old fallow covered with natural meadow vegetation. Soil monoliths were placed in wooden boxes of 20 * 20 * 30 cm in size. In a laboratory, each monolith side was firmly stuck to the appropriate box wall with hot paraffin. This method permitted us to avoid "side effects" upon the percolation of water and solutions through a monolith. The monolith bottom was also covered with paraffin and then perforated for free penetration of solutions.

Before the experiment started, all plants in the monoliths had been cut at the soil surface level. The chloride solution of ^{137}Cs was evenly added to the monolith surface; its volume was equal to 100 ml and the total activity, to 0.1 MBq. This solution portion was completely consumed by the soil. Then, water was added in 2-1 portions once in two or three days. In this case, all added water was completely absorbed by the soil. Next, the monoliths were watered for two-four weeks in a volume equivalent to 400 mm precipitation. The experiment was performed in the light at a temperature of 22-25 °C. Plants germinated partially during the watering period. Eluate samples did not contain ^{137}Cs . Simultaneously, a similar experiment was performed with the water-saturated column of disturbed soil with extracted roots sieved through a 2-mm mesh. After the end of the washing period, the integral distribution of ^{137}Cs in the column was studied, as well as its distribution at the aggregate level in the undisturbed soil columns.

In addition to special tests on the initial ^{137}Cs distribution in the soils, we studied the ^{137}Cs concentration gradients and its localization in the undisturbed soil sampled in the areas moderately contaminated by the Chernobyl-derived fallout.

The results obtained for two sampling points are discussed in this paper: (1) loamy soddy-podzolic soil under pasture (analogue of the soil used in the laboratory experiments) near the village of Afanasovo, Ulianovsk district, Kaluga oblast and (2) podzolized heavy-loamy chernozem under meadow near the settlement of Krasnoe, Plavsk district, Tulaoblast. The samples were collected in summer 2000, i.e., 14 years after the Chernobyl fallout.

The distribution of ^{137}Cs in the columns, as well as in separate soil and plant samples, was measured by a Compugamma 1282 LKB spectrometer (Sweden).

The direct scraping of the aggregate surface with a subsequent analysis of the soil mass separately from the intrapedal masses is used to study the distribution of toxicants or any other substances over the surface of soil aggregates and in the intrapedal mass [1,2].

Foreign researchers made attempts to improve and standardize the procedure for sampling the surface of soil aggregates. For this purpose, wet aggregates were frozen in

liquid nitrogen (-196°C) and then washed on sieves at positive temperatures. The thawed surface film was washed off, collected, and analyzed [3].

We have also applied similar, though simpler approaches. However, the autoradiography method using radionuclides or other toxicants with radioactive isotopic tracers appears to give the most vivid idea on the initial distribution of labeled compounds in the soil. An autoradiographic image represents an X-ray replica of the tracer obtained from the contact of the studied object with the X-ray film for a certain period. This method is widely used in experiments with plants, as well as in paper or thin-layer chromatography; however, we are unaware of its application in soil science. The obtaining of autoradiographic images of soil samples is complicated to some extent by the necessity of getting a flat cut (with an area reaching in some cases several hundred cm²) without disturbing the natural soil structure. For this purpose, the soil was saturated with paraffin by the slow plunging of dried samples into molten paraffin at a temperature of about 100°C. The cooled samples were cut into several 1-cm-thick plates. The surface destined for autoradiography was additionally treated with a sharp knife to remove a 0.1- to 0.2-mm-thick layer of paraffin-saturated soil. This measure was necessary to remove molten particles of paraffinized soil from the cut surface.

The contact with an X-ray film can be achieved in any rigid light-tight box. The contact closeness can be increased by inserting the layers of elastic porous substance (for example, foam-rubber) from the sides of the film and the sample. The duration of exposure is either calculated by standard procedures [5] or is selected empirically.

In addition to autoradiography, we washed off the surface layers of aggregates on a sieve by the repeated plunging of samples into water. For this purpose, aggregates of any size (but no less than 3 mm) collected from the air-dry undisturbed soil sample were placed on a 1-mm sieve. This sieve was plunged into the water several times; the number of these plunges was experimentally established; this number depends on the thickness of the surface layer that has to be removed from the aggregates. This method permitted us to subdivide aggregates into the necessary number of layers.

The discussion above concerns direct methods for the determination of studied substances in different parts of soil aggregates. Along with them, we have also used an indirect method of ¹³⁷Cs determination in aggregates of different sizes obtained from sieving air-dry soil samples. If we assume that a toxicant mainly accumulates in the surface layers of the aggregate, the toxicant concentration per soil mass unit should rise with a decrease in aggregate size due to the growing specific surface.

Finally, to understand the formation of initial gradients of ¹³⁷Cs concentrations in the soil, it is necessary to additionally find the content of this radionuclide in root residues. For this purpose, we picked up roots with pincers upon the sieving of dry samples and washing of aggregates on a sieve. In this case, the only problem was to determine the ¹³⁷Cs concentration in plant residues without taking into account the total element content in the given form.

Results and discussion

Figure 1 shows the averaged data on vertical distribution of ¹³⁷Cs in aggregated and disintegrated soil columns. The soil in the columns also differed in its initial moisture. The moisture of aggregated soil was equal to $60 \pm 5\%$ of the total moisture capacity, which provided the manifestation of aggregated soil properties, i.e., fracturing and accessibility of the aggregate surface to the washing water, as well as the relatively easy percolation of water through the column.

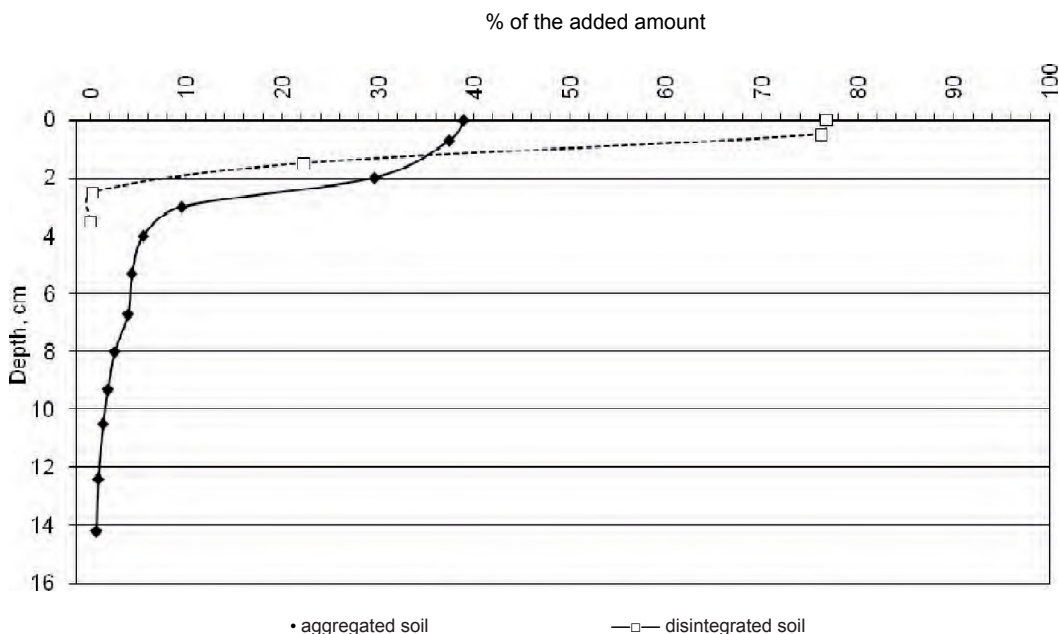


Fig-1 . Vertical distribution of ^{137}Cs in aggregated and disintegrated soil. The washing rate corresponds to 400-mm precipitation in both cases

The disintegrated soil column was preliminarily saturated with water. Because of destroyed aggregates, filtration was very slow, even at the pressure of a 500 mm water column.

The total depth of ^{137}Cs penetration did not exceed 2 cm in the disintegrated soil¹. In the aggregated soil, a noticeable amount of ^{137}Cs was registered at depths of less than 10 (several fractions of a percent of the added amount) and 20 cm (tenths of percent). The formation of zones of elevated radionuclide concentration in fissures and interaggregate spaces with only a part of the soil sorption capacity being spent for the ^{137}Cs retention seems to be one of the principal reasons for a more intense ^{137}Cs migration in the aggregated soil.

The autoradiographic replicas (figs. 2, 3) obtained from scanning and computer processing of images provide a clear idea about the initial distribution of ^{137}Cs in the studied soils.

Judging from fig. 2, the total depth of ^{137}Cs penetration into the aggregated soil column and the pattern of its general distribution in this column are in agreement with radiometric data (fig. 1). Distinct localization of the radionuclide on the surface of aggregates of different sizes is notable. Dark irregular mottles are probably formed in places where the faces of several individual aggregates or their parts merge together at the surface of the cut or in places with accumulations of small (<1 mm) aggregates. In addition, note that ^{137}Cs is mainly localized on the aggregates of relatively small size (up to 2-3 mm); thus these aggregates are responsible for the formation of initial concentration gradients of ^{137}Cs in the soil.

¹ It took water one month to penetrate into the column upon its permanent filtration in an amount equal to a 400 mm water column.

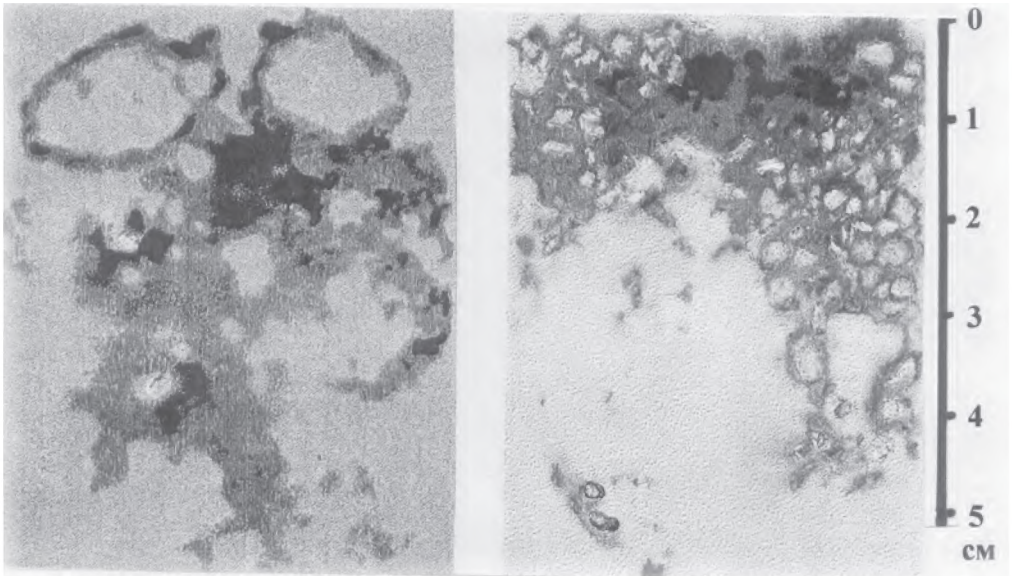


Fig. 2. Radioautography of initial ^{137}Cs distribution in the undistributed soil

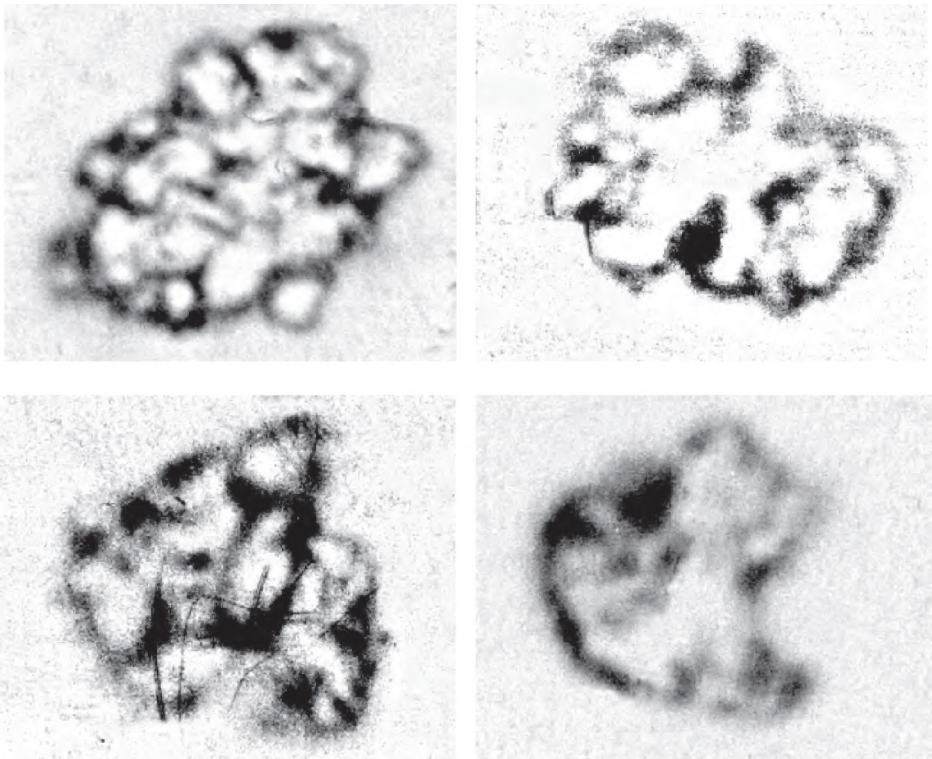


Fig. 3. Autoradiography of cuts of arbitrary soil aggregates contaminated with ^{137}Cs

Figure 3 shows the autoradiographic replicas of cuts of four arbitrary aggregates 1.0-1.5 cm in size, patterns show that ^{137}Cs in many cases is localized only on the surface of selected aggregates but all the surface of finer structural units composing a 1 aggregate. This suggests that relatively small aggregates (less than 2-3 mm in size) are probably the stable structural components in the studied soil. In general, this complies with the view on the aggregate distribution in similar soils [6].

The specificity of surface localization of ^{137}Cs analyzed by the successive washing of aggregates sieve. Four aggregates of 1.6-2.3 g (the average was equal to 1.945 g) were arbitrarily collected for this purpose. The results obtained are given in table 1.

Table 1

The initial distribution of ^{137}Cs in different layers of a soil aggregate washed off from this aggregate on a sieve. The thickness of layers is calculated for a conventional spherical aggregate with a mass of 1.945 g and bulk density of 1.3 g/cm³

Number of the layer washed off from the soil aggregate	Layer mass, g	Layer thickness, mm	Total layer activity, Bq*	^{137}Cs distribution by layers по слоям, % of the sum
1, surface	0,253	0,39	338	43,1
2	0,310	0,54	204	26,0
3	0,343	0,69	115	14,7
4	0,208	0,50	39	5,0
5	0,113	0,31	16	2,0
6	0,225	0,73	33	4,2
7	0,115	0,46	13	1,7
8, central part	0,378	4,98**	27	3,4
Total	1,945	8,60	785	100

* The radiometry error does not exceed 5%.

** The radius of the central aggregate part retained by the sieve upon washing.

As the actual area of the selected aggregates more so, their total area participating in the initial sorption of ^{137}Cs are unknown, we may just approximately assess the thickness of layers participating in the initial radionuclide retention. For calculation, we have conventionally assumed that all four aggregates are spherical, i.e., their surface area is minimal. In doing so, deliberately overestimate the absorption layer thickness, probably, by several times, taking into account that intrapedal surfaces also participate in sorption processes.

As proceeds from table 1, about 70% of the activity of ^{137}Cs retained by the aggregates is concentrate the first and second successively washed layers, total thickness of which for a conventional aggregate constitutes about 1 mm. For an actual aggregate, thickness of layers initially accumulating radionuclides should constitute several fractions of a millimeter (at present, more precise estimates cannot be done).

According to the data in table 1, the values of linear specific activities were calculated for all washed aggregate layers in Bq/mm, and the curve of the in linear distribution of ^{137}Cs in the conventional glob soil aggregate was built to demonstrate the spatial pattern of ^{137}Cs more vividly. However, the surface actual aggregates exceeds that of a sphere by several times, and the peak of localization on the aggregate surface should be several times narrower to constitute tenths of mm. Hence, the initial concentration gradients should be correspondingly higher.

We performed comparative studies of ^{137}Cs distribution by the successive washing of aggregates on a sieve using samples contaminated with ^{137}Cs for 14 years after the Chernobyl accident. Recall that the samples were collected in the moderately contaminated areas Kaluga and Tula oblasts. All analyzed samples manifested virtually uniform distribution of the radionuclide in the aggregates. The successive washing of these aggregates on a sieve showed no gradients in the ^{137}Cs concentration at the aggregate level. The problem of the ratio between diffusive and destructive mechanisms of ^{137}Cs redistribution at the aggregate level of soil arrangement remains unstudied, as well as the problem of the rates of these processes.

As noted above, we assessed indirectly the initial localization of ^{137}Cs on the surface of aggregates by determining the content of the radionuclide in the samples prepared from dispersed aggregates of different sizes. The results of this determination are given in table 2. They prove that the radionuclide concentration rises approximately by an order of magnitude with a decrease in the aggregate size from 10 to 0.5 mm and a corresponding increase in the specific surface values; this regularity is preserved at different depths within the contaminated soil layer.

Table 2

The ^{137}Cs distribution in soil samples prepared from aggregates of different sizes Bq/g soil

Depth, cm	Fraction, mm						
	>10	5-10	3-5	2-3	1-2	0,5-1	<0,5
0-2	384	241	655	1301	1883	2816	2153
2-4	11,4	31,9	23,5	28,7	63,1	85,7	94,7
4-6	2,3	3,9	3,4	4,4	7,4	10,2	14,6
6-8	0,57	0,55	1,13	2,06	1,97	3,93	7,24
8-10	0,34	0,34	0,98	0,58	1,28	3,09	4,87

This technique turned out to be very sensitive to revealing initial concentration gradients; therefore, we tried to apply it to the samples contaminated by the Chernobyl fallout (table 3). The results obtained manifest a very weak tendency for an increase in the ^{137}Cs concentration in the aggregates of less than 1 mm in size. However, in this case, fine aggregates might have been enriched in ^{137}Cs due to physical contamination of this fraction with clay particles upon dry sieving. The clay fraction is known to absorb Cs most intensely.

Disappearing gradients of the initial concentration of ^{137}Cs on soil aggregates may be one of the reasons for damping intensity of ^{137}Cs absorption by plants in the zone contaminated by the Chernobyl fallout [7]. These issues require further investigation. Summing the results obtained, let us compare the concentration effects and radionuclide concentration gradients forming in different parts and components of soil. For this purpose, we introduce the relative value, the so-called concentration coefficient (K_c), which represents ratio between the toxicant concentration (or radionuclide specific activity) in any specified soil component (aggregate surface layer, aggregate fraction of definite size, root remains, etc.) and weighted average toxicant concentration in (or specific activity of) the soil lay horizon, to which the studied component belongs to. The concentration effect as regards the weighted average content of substance is registered if $K_c > 1$.

Table 3

The distribution of ^{137}Cs in soil aggregates of different sizes from soil samples collected in the area contaminated by the Chernobyl fallout

Sampling place	Depth, cm	Fraction, mm	Specific activity*, Bq/g
Kaluga oblast, the village of Afanasovo, pasture, soddy-podzolic soil	5-15	<0.25	0.63
		0.25-1	0.58
		1-2	0.49
		2-3	0.54
		3-5	0.50
		5-10	0.39
		> 10	0.39
Tula oblast, the settlement of Krasnoe, forest shelter belt, chernozem	0-5	<0.25	0.80
		0.25-1	0.48
		1-2	0.51
		2-3	0.54
		3-5	0.46
		5-10	0.45
		10	0.47

The values of K_c obtained in our experiments shown in table 4. In the surface soil layer (0-2 cm) approximately equal concentration effects are observed in roots, the surface aggregate layer, and, in the fraction containing aggregates <1 mm in size and microaggregates. At the depths from 2-4 to 4-6 cm, the effect of radionuclide concentration on the aggregate surface (fraction <1 mm) becomes less pronounced though is still preserved ($K_c > 1$); however, the relative concentration of ^{137}Cs in roots grows sharply. It does not mean that the bulk of Cs is contained in roots at a depth of 6 cm, since the mass of mineral soil exceeds the mass of roots at this depth by several

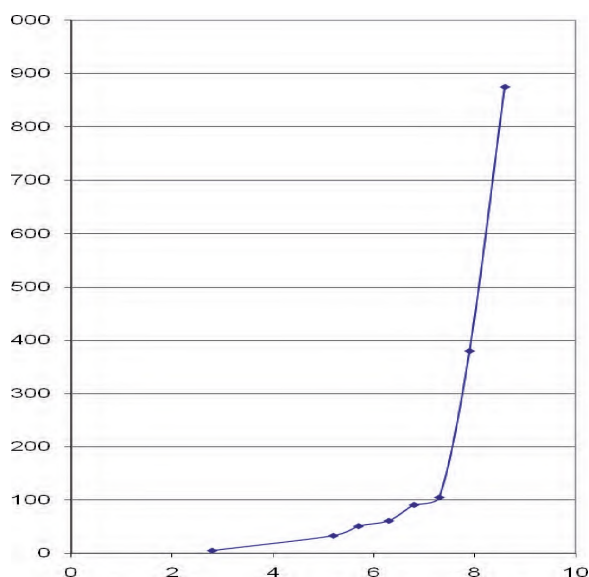


Fig. 4. Initial distribution of ^{137}Cs by conventional spherical aggregate. The zero point fits the aggregate center

Table 4

Values of ^{137}Cs concentration coefficients in root residues, surface layers of soil aggregates, and in different aggregate-size fractions

Depth, cm	Root residues	Surface layer (0.39 mm) of soil aggregates	Fractions, mm						
			>0,5	0,5-1	1-2	2-3	3-5	5-10	<10
0-2	3,4	3,3	2,2	2,9	1,9	1,3	0,68	0,25	0,39
2-4	12,3	—	1,5	1,3	1,0	0,45	0,37	0,50	0,18
4-6	108	—	1,1	0,8	0,57	0,34	0,26	0,30	0,18

hundred times. However, an increase in the ^{137}Cs concentration effects in root residues with increasing depth of sampling attests to the importance of roots in the vertical migration of ^{137}Cs . Assuming that a significant portion of root mass concentrates in the interaggregate space, we may assume that roots participate in the formation of concentration gradients on aggregate surfaces due to root exudates containing ^{137}Cs and due to the redistribution of this radionuclide upon the decomposition of root residues.

Conclusions

When aggregated soils are contaminated by ^{137}Cs , substantial gradients of the ^{137}Cs concentration and activity are formed at the surface of soil aggregates as a result of initial sorption processes. Initially, only a part of the soil adsorption complex participates in sorption processes that develop on the surface of soil aggregates; this favors vertical migration of ^{137}Cs in the soil profile (mainly, through interaggregate pores) and its uptake by plants. In the nonaggregated soil, these processes are less intensive.

Autoradiography of undisturbed soil samples, successive washing of aggregates on sieves, and the measurement of pollutant concentrations in aggregate fractions of different sizes appear to be efficient methods to study the accumulation of ^{137}Cs on the surface of soil aggregates.

The successive aggregate washing proves that the initial thickness of the ^{137}Cs -absorbing layer constitutes fractions of a millimeter in heavy loamy soddy-podzolic soil. Autoradiography provides overestimated data on the thickness of this layer because of the penetrating capacity and irradiation effect on the photosensitive layer not only in the zone of direct contact with the radioactive substance but also at some distance from it, which is equal to several tenths of a millimeter in the case of ^{137}Cs radiation.

Autoradiography shows that ^{137}Cs is predominantly adsorbed on the surface of aggregates of less than 2-3 mm in size and, probably, microaggregates. This method permits us to assess the contribution of aggregates of different sizes and different parts of aggregates to the sorption of the toxicant.

The assessment of the initial ^{137}Cs concentration in the soil structural components at a depth of 0-2 cm in relative units (concentration coefficients, K_c) attests to approximately equal K_c values in the root mass, the surface (0.4-mm-thick) layer of large (>1 mm) aggregates, and fine (<1 mm) aggregates and microaggregates. The values of K_c in root residues are higher by one or two orders of magnitude in the soil layers of 2-4 and 4-6 cm, respectively, which attests to the role of living plants and their roots in the vertical redistribution of ^{137}Cs upon the aerial supply of the radionuclide on the soil surface in the period of active plant growth.

In the soil samples collected 14 years after the Chernobyl fallout, the concentration gradients have almost disappeared at the aggregate level. A decreasing intensity of ^{137}Cs intake by plants, which is observed in the zone contaminated by the Chernobyl fallout, appears to be one of the significant effects of this phenomenon.

The idea about the initial localization of toxicants on the surface of soil aggregates may help researchers in distinguishing between recent and background contamination in a number of

cases (for example, for heavy metals). It can be supposed that natural background contamination (or contamination in the past) is not accompanied by concentration gradients of a contaminant at the surface of soil aggregates (the contaminant is evenly distributed in the aggregate mass, at least, within the biologically active surface soil layer).

In addition, the preparative separation of structural soil components accumulating toxicants during the initial period of their interaction with soil together with the subsequent analysis of separated component may increase substantially the sensitivity of determination of the toxicant content in the soil.

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ПЕРВИЧНОЕ ВЗАИМОДЕЙСТВИЕ РАДИОЦЕЗИЯ С КОМПОНЕНТАМИ ПОЧВЫ ПРИ АЭРАЛЬНЫХ ВЫПАДЕНИЯХ

Аннотация: получено прямое и косвенное экспериментальное подтверждение первичной локализации ^{137}Cs на поверхности почвенных агрегатов. Выполнена приближенная оценка толщины поверхностного сорбирующего слоя. Методом радиоавтографии получена общая картина распределения ^{137}Cs на агрегатном уровне в условиях горизонта А1 дерново-подзолистой тяжелосуглинистой почвы ненарушенного сложения. Обсуждены возможные следствия формирования первичных градиентов концентрации ^{137}Cs в почвах.

Ключевые слова: почвенные агрегаты, радиоавтография, радиоцезий, коэффициент концентрирования, дерново-подзолистая почва, внутриведная масса, первичные градиенты концентрации.

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