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Chapter 3

Influence of the Clay Fraction Mineralogy of Soils and Agromeliorants on ^{137}Cs Mobility in Soils and Accumulation in Plants

Vyacheslav S. Anisimov, Natalya I. Sanzharova*, Lyudmila N. Anisimova, Andrey I. Sanzharov, Dmitry V. Krylenkin, and Rena A. Mikailova

Russian Institute of Radiology and Agroecology of National Research Centre, Kurchatov Institute, Obninsk, Kaluga Oblast, Russia

**natsan2004@mail.ru*

Abstract

In order to effectively address the optimization of remediating agricultural lands affected by nuclear accidents, thorough research on the parameters of radionuclide accumulation by crops and the factors that influence this process is necessary.

The mobility of radionuclides in soil is affected by a number of factors, including the granulometric composition of soils. Soils with high-dispersed particles are characterized by a high absorption capacity. Differences in the ability to fix radionuclides are associated with the mineralogical composition of the mechanical fractions of the soil. The ability of soils to fix ^{137}Cs is largely determined by the content of labile clay minerals in the soil.

The development of remediation techniques for contaminated soils relies on effectively regulating the processes of sorption/fixation of ^{137}Cs. These techniques involve the use of agromeliorants (sorbents) to minimize the mobility of the radionuclide in the soil–plant system. The physicochemical processes of the interaction between agromeliorants (sorbents) and soil, as well as the behavior of chemical analogues such as potassium (K), play a crucial role in understanding how these substances influence the transfer of radionuclides, particularly ^{137}Cs.

This chapter presents the findings of a series of comprehensive studies that examine how the mineral composition of soil's clay fraction affects the behavior of ^{137}Cs, investigate the migration parameters of the isotopes ^{137}Cs and ^{40}K from soil to pasture grasses, and analyze the impact of agromeliorants on the biological mobility of ^{137}Cs in soil using radiocesium interception potential.

Keywords: ^{137}Cs, bioavailability, soil, granulometric composition, mineralogy, agromeliorants.

1. Introduction

A large-scale nuclear accident can result in radioactive contamination of vast agricultural areas, which will severely affect agricultural production and lead to significant social and economic consequences. Remediation of contaminated agricultural land is one of the important problems in mitigating the consequences of radiation accidents. The success of remediation is influenced by numerous factors, such as soil and plant characteristics, land use systems, and the time elapsed since the incident. In order to effectively address the challenges associated with optimizing the remediation of agricultural lands affected by nuclear accidents, it is crucial to thoroughly investigate the accumulation parameters of radionuclides in crops and identify the key factors that influence this intricate process.

Among man-made radionuclides, ^{137}Cs is one of the most environmentally significant. It was present in both the global fallout and the Chernobyl nuclear accident. The mobility of radionuclides in soil is affected by a number of factors, including the granulometric composition of soils. As the size of soil particles decreases, the absorption of ^{137}Cs by the soil increases due to the greater total surface area of the particles. Soils containing highly dispersed particles (<0.001 mm) have a high absorption capacity. Differences in the ability to fix radionuclides are associated with

the mineralogical composition of the mechanical fractions of the soil. The coarse-grained fractions are mainly composed of primary minerals such as quartz, feldspars, and micas, which have a limited absorption capacity. In contrast, the finer fractions are dominated by secondary clay minerals such as montmorillonite, kaolinite, and hydromica, which have a significantly higher absorption capacity. According to Aleksakhin *et al.* (1992), the minerals are arranged in the following sequence based on the strength of radionuclide fixation, from strongest to weakest: ascanite, hydrophlogopite, phlogopite, gumbrine, vermiculite, bentonite, kaolinite, vivianite, hydrogoethite, biotite, muscovite, and damurite.

The capacity of soils to capture and retain ^{137}Cs is primarily influenced by the presence of easily exchangeable clay minerals in the soil composition (Cremers *et al.*, 1988). Physicochemical processes play a crucial role in the behavior of ^{137}Cs in soils and its transfer to plants. These processes include both the ion exchange binding of ^{137}Cs and its non-exchangeable sorption (fixation) by the soil's solid phase. Selective sorption and non-exchangeable sorption (fixation) by the solid phase of soils are typical for ^{137}Cs.

In accordance with widely accepted principles, the presence of illite (hydromica) clay minerals with a 2:1 crystal lattice plays a crucial role in determining the fixation of ^{137}Cs in soil. Hydromicas are silicates composed of layers of silicon dioxide tetrahedra and aluminum hydroxide octahedra. They exhibit isomorphic substitutions of Si^{4+} and Al^{3+} cations within the crystal lattice with cations of lower charge. When a lattice is formed, it creates a negative charge within it. This negative charge is then balanced out by the presence of K^+ ions, primarily some NH_4^+ ions, which occupy the hexagonal voids in the tetrahedral layers of two neighboring packets. Due to weathering, the lattice of the clay mineral loses the interlayer K^+ at the ends of the layers. When K^+ exits the interpacket space, a negative surface charge emerges, causing mutual repulsion and expansion of the two adjacent layers at the ends. The enlarged wedge-shaped regions of the two neighboring areas are distinguished by their high selectivity for K^+, NH_4^+, and, especially, Cs^+.

The theory of selective sorption originated from understanding and describing the complex processes of interaction between radionuclides and soil. This theory categorizes three types of ion exchange sorption sites for Cs^+ based on their level of selectivity: non-selective sorption centers on particle surfaces (regular exchange sites, RES), sorption centers on the expanded edge areas of interlayer spaces in layered clay minerals

(frayed edge sites, FES), and highly selective centers (high-affinity sites, HAS) (Bolt *et al.*, 1963; Cremers *et al.*, 1988).

Regulating the sorption/fixation processes of ^{137}Cs is crucial for developing effective methods to remediate contaminated soils. To achieve this, agromeliorants (sorbents) are utilized to minimize the mobility of radionuclides in the soil–plant system. The physicochemical processes of agromeliorants' (sorbents') interaction with the soil and the behavior of chemical analogs, such as potassium, play a crucial role in determining the influence of agromeliorants on the mobility of radionuclides, particularly ^{137}Cs.

Agromeliorants, such as sorbents and potash fertilizers, have a significant impact on the biological mobility of ^{137}Cs in soil. This impact is determined by the radiocesium interception potential (RIP), which is calculated by multiplying the capacity of FES and the selectivity coefficient of Cs^+ in relation to K^+ during exchange on FES. The distribution coefficient K_d is the key indicator of how radionuclides are distributed between the solid and liquid phases of soil. It is determined by the ratio of the radionuclide's equilibrium concentration in the solid phase to its concentration in the solution (Sheppard, 1985). RIP and K_d values vary greatly and help to understand how different factors affect the mobility and availability of ^{137}Cs in various types of soils. This includes the use of agromeliorants in the recovery of contaminated soils.

2. Influence of the Granulometric and Mineralogical Composition of Soils on the Mobility of ^{137}Cs in the Soil–Plant System

By conducting a radioecological survey on lands in the European part of Russia, we were able to determine the migration indicators of artificial radionuclide ^{137}Cs in the "soil–pasture plants" system of both the areas affected by the Chernobyl accident and unaffected areas. This study covered a range of natural and seminatural ecosystems, thus providing valuable insights. The most crucial migration parameters under study are the coefficients for radionuclides transferring from soil to plants. This transfer is quantified using the aggregated transfer factor, expressed as $T_{ag} = [^{137}Cs]_{plant}/[^{137}Cs]_{soil}$ (Bq kg^{-1})/(Bq m^{-2}). T_{ag} is necessary for evaluating how well soils can buffer against radionuclides and how effective countermeasures are in minimizing the transfer of ^{137}Cs to crops.

By using the T_{ag} parameter, it is also possible to assess the impact of the main physical and chemical characteristics on the soil's buffering capacity, which affects the accumulation of radionuclides by plants.

In relation to ^{137}Cs, soil properties such as granulometric and mineralogical composition are of particular interest. Regarding this matter, the mineral composition of the clay fraction of soils (<0.001 mm) appears to have a crucial impact on the movement of radionuclides in the soil. According to some studies (Sposito, 2008; Sokolova and Trofimov, 2009), the main factors determining the absorption capacity of soils are the clay fraction and humus. Since Cs^+ cations do not form complexes with specific soil organic compounds, their sorption by ion exchange in the organic matter is non-selective, leading to easy desorption into the soil solution and subsequent selective absorption by mixed-layer clay minerals (Brouwer *et al.*, 1983; Cremers *et al.*, 1988; Hird, 1995, 1996). Therefore, the granulometric composition and mineralogical composition of soil, specifically the abundance of elementary clay particles, are the key factors that determine the migration ability of a radionuclide in the soil–plant system.

In order to verify the corresponding hypothesis and determine the quantitative parameters of the relationships $T_{ag} = f$(clay content, %) and $T_{ag} = f$(clay mineralogical composition) for several important sites, we analyzed not only the granulometric composition of the soils but also the mineralogical composition of the clay fraction. To date, detailed studies have been carried out on six key sites within the Eastern European plane (Table 1).

In the Ulyanovsk district of the Kaluga region, there were four key areas affected by the Chernobyl accident. On the lands next to the Vytebet River, two soil-geomorphological profiles were created. These profiles covered watersheds, terraces, and floodplains on both slopes of the river valley, lying from west to east. The profiles cross vast territories adjacent to the river and characterize the forms of their macro- and mesorelief.

The research area in the lower part of the Vytebet River is located along the route Efimtsevo–Zhukovo–Smetskaya Village (which is now destroyed). The route is marked as route 1 and has two sampling sites: No. 1–1 and No. 1–2. Upstream of the Vytebet River, route 2 was laid, along which sampling sites No. 2–1 and No. 2–2 are located.

The first profile (route 1) is laid in the lower reaches of the Vytebet River. Sampling site 1–1 is located on the left side of the Vytebet River valley in the watershed (Ulyanovsk Opole). The primary soil type in the

Table 1. Locations of key areas with sampling sites.

Key areas, #	**(1–1)**	**(1–2)**	**(2–1)**	**(2–2)**	**3**	**4**
Region, Geographical coordinates	Kaluga region, Ulyanovsk district, Efimtsevo village, left side of Vytebet River valley N: 53°47′17″ E: 35°35′39″	Kaluga region, Ulyanovsk district, Zhukovo village, right side of Vytebet River valley N: 53°47′21″ E: 35°39′19″	Kaluga region, Ulyanovsk district, Yagodnoe village, right side of Vytebet River valley N: 53°33′45″ E: 35°38′11″	Kaluga region, Ulyanovsk district, Yagodnoe village, left side of Vytebet River valley, second terrace N: 53°33′43″ E: 35°37′03″	Kaluga region, Peremyshlsky district, experimental field of the Kaluga Agricultural Research Institute N: 54°25′33″ E: 36°04′55″	Kursk region, Central Black Earth State Natural Biosphere Reserve named after Professor V.V. Alekhin N: 51°34′15″ E: 36°05′41″
Soil	Sod-podzolic sandy loam	Sod-podzolic loamy sand	Light-gray forest loam	Light-gray forest sandy loam	Gray forest clay loam (Greyzemic Phaeozem Albic)	Chernozem typical clay loam (Haplic Chernozem)

watershed at site 1–1, which is 212 m above sea level, is sod-podzolic sandy loam with a loamy cover.

Sampling site 1–2 was found on the upper terrace of the right side of the Vytebet River valley, next to a coniferous forest. This forest is part of a large, well-preserved forest area called "Zasechnaya Cherta" (Abatis Border), located in the Kaluga Zaseki Nature Reserve, specifically in the Oksko-Vytebetsky natural geographical area. The soil is sod-podzolic loamy sand, formed on binomial deposits known as fluvioglacial sands on the carbonate Dnieper moraine.

The second geomorphological profile (route 2) is located in the middle section of the river near Yagodnoye Village. It goes from west to east, crossing watersheds, terraces, and the river's floodplain. The main soil type on terraces near the watershed in this geographic area is a light-gray forest soil with various particle sizes, ranging from clay loam to loamy sand. These soils are formed from layers of loam and sand from glacial deposits. Sampling point 2–2 is located on the second terrace on the left bank of the Vytebet River. It corresponds to the light-gray forest sandy loam soil.

On the other side of the Vytebet River valley, there are meadows on terraces next to the Zasechnaya Cherta forest area in the Kaluga Zaseki Nature Reserve. Sampling point 2–1 was located in a meadow area. It is a light-gray forest loam soil that developed on binomial deposits, specifically a thin layer of fluvioglacial sands on the carbonate Dnieper moraine.

The research was carried out in the chernozem key area, located within the picturesque landscape of a hilly plain, 500 m away from the village of Zapovedny. This area falls within the boundaries of the Central Black Earth State Natural Biosphere Reserve, named after Professor V.V. Alekhin (site "Streletskaya Steppe"), in the Kursk region, at coordinates N 51°34′14.75″ E 36°05′40.50″.

The key area was established on gray forest soil in the experimental field of the Kaluga Research Institute of Agriculture, located in the Peremyshlsky district of the Kaluga region.

Sampling sites for soil and pasture grass (cereal) plants were carefully selected following the methodological guidelines of the IAEA (Dercon, 2022). Soil samples were taken from different layers (0–5, 5–10, 10–15, and 15–20 cm) in a specific area of a protected natural territory (Central Black Earth State Natural Biosphere Reserve). The square method was used for sampling, with samples taken at the corners and center of a 10×10 m^2 area. A drill core sampler, specially designed for layered soil

sampling, was used (Patent No. 2657555 by Kursk Federal Agricultural Research Center). The diameter of the working part of the drill core sampler with the sample container is 100 mm. This drill has a unique feature: It can not only collect soil material from a specific layer but also estimate the density of the soil composition in that layer. The soil in the study area was classified as chernozem typical clay loam (Haplic Chernozem, WRB 2014).

Soil samples were taken from different layers at key sites, as mentioned above, as well as from the topsoil. A radiological ring with a diameter of 14 cm and a height of 5 cm was used for sampling (Dercon, 2022). Layered soil sampling was carried out simultaneously with the collection of conjugate plant samples.

The physical and chemical properties of the soil (Table 2) were determined using standard methods (Vadyunina and Korchagina, 1986; Mineev, 2001; Pansu and Gautheyrou, 2006): pH_{KCl} (pH_{H2O}) — potentiometric in a soil suspension in 1 M KCl solution (distilled water) at a solid-to-liquid ratio of 1:2.5; organic carbon content — by Tyurin's wet oxidation method (Tyurin, 1931) using potassium dichromate and concentrated sulfuric acid and by the Dumas method (Pansu and Gautheyrou, 2006) using a carbon analyzer model AN-7529 (Republic of Belarus); hydrolytic acidity — according to Kappen; the sum of absorbed bases — according to Kappen–Gilkovitz; and the exchangeable forms of K, calcium (Ca), and magnesium (Mg) were extracted from the soils using 1 M NH_4Cl (pH 6.5).

The specific activity of radionuclides in soil and vegetation was determined using gamma-spectrometry using a Gamma–1P spectrometer with a semiconductor detector made of ultrapure germanium with a relative registration efficiency of 35%. Dust particles were previously removed from dried plants (by type) by treating them with compressed air in a cyclone chamber. Bags made of a Petryanov fabric (FPP-15-1.5) were used as filters to trap dust particles in the cyclone.

The particle-size distribution of the soils was determined by sedimentation using a SediGraph III 5120 (Particle Size Analysis System) apparatus. The sample was first dispersed by an ultrasonic disperser at a power of 120 W in 50 ml of dispersant solution (1% sodium pyrophosphate, $Na_4P_2O_7$) for 10 minutes.

The mineralogical composition of the clay fraction (<1 μm) in the soils under investigation was determined through X-ray diffractometry at the Department of Soil Chemistry, Lomonosov Moscow State University.

Table 2. Physicochemical properties of the studied soils.

Key areas, #	(1–1)	(1–2)	(2–1)	(2–2)	3	4
Mass fraction of particles (mm) in soil, %	—	—	—	—	—	—
1–0.25	4.14	72.06	5.9	8.57	10.70	—
0.25–0.05	9.82	2.50	3.2	13.60	1.67	2.58
0.05–0.01	60.29	8.48	54.4	49.92	35.23	38.48
0.01–0.005	6.90	4.22	13.0	7.68	8.27	9.73
0.005–0.001	8.44	6.05	15.7	10.70	11.93	11.53
<0.001	10.41	6.68	7.8	9.54	32.20	37.73
Sum of fractions	74.26	83.04	63.50	72.09	47.60	41.05
>0.01 mm	25.74	16.96	36.50	27.91	52.40	58.98
<0.01 mm						
pH (KCl)	5.07 ± 0.05	3.94 ± 0.02	5.19 ± 0.04	6.28 ± 0.04	5.71 ± 0.02	5.40 ± 0.07**
Hydrolytic acidity, cmol(+) kg^{-1}	2.44 ± 0.34	6.06 ± 0.15	0.67 ± 0.04	4.38 ± 0.21	—	6.55 ± 0.04
C_{org}, %	1.47*	1.33*	1.88*	1.40*	—	4.88 ± 0.49
CEC, cmol(+) kg^{-1}	8.37 ± 0.25	5.89 ± 1.21	15.14 ± 5.34	7.11 ± 0.40	—	48.0 ± 0.3
The content of exchange cations, cmol(+) kg^{-1}	—	—	—	—	—	—
Ca^{2+}	5.29 ± 0.19	2.35 ± 0.08	8.27 ± 0.32	2.32 ± 0.20	—	11.46 ± 1.63
Mg^{2+}	1.12 ± 0.04	0.40 ± 0.01	4.31 ± 0.18	0.48 ± 0.02	—	1.39 ± 0.21
K mobile, mg kg^{-1}	168 ± 9	175 ± 15	269 ± 20	153 ± 3	—	123 ± 68

Note: *It was determined by the dry ashing method according to Dumas. **pH (H_2O) = 6.29 ± 0.07.

Initially, the clay fraction of the soils underwent saturation with Ca or Mg, followed by mineralogical analysis using X-ray diffractometry on the DRON-3 device. Quantitative determination of illite, kaolinite, the amount of chlorite, and labile minerals (expressed as a percentage of the sum of these three components) was carried out utilizing a modified method developed by E. A. Kornblum (Sokolova *et al.*, 2005). The X-ray diffractometry parameters were set as follows: the BSV-29 tube (Cu) mode is 20 mA and 35 kV, with a Ni filter, Soller slits — vertical 1.00 mm and horizontal 8.00 mm. The diffractometer was equipped with a scintillation detector with following parameters: lower limit 200 s^{-1}, upper limit 2500 s^{-1}, photomultiplier (PMT) gain — 4.0, voltage on the PMT divider — 720 V, Soller slits — vertical 2.00 mm and horizontal 16.00 mm. The shooting method involved powder with a 2-theta range; combined time of 3.000s, and a V (velocity) of 4.0 g/min.

Throughout the study, the primary physicochemical parameters for the upper layer (0–20 cm) of the examined soils, including pH, hydrolytic acidity, cation exchange capacity, and the content of exchangeable Ca, Mg, and K, were determined. These determinations were carried out following well-established and widely accepted analytical methods (Arinushkina, 1970; Mineev, 2001). The granulometric and mineralogical composition of the soils under investigation is detailed in Tables 2 and 3.

A recurring observation in the course of our research is the strong correlation between physicochemical indicators in the upper soil horizons and the distinctive features of their granulometric composition. The granulometric composition, in turn, is influenced by the lithological composition of meter-thick unconsolidated rocks from the Quaternary Period, surfacing and serving as the substrate for the formation of the respective soils. The binary nature of the soil-forming rocks is a prevalent characteristic in the studied region, particularly at key sites 1–1, 1–2, 2–1, and 2–2.

In these areas, moraine or cover loams are covered by a thin layer (up to 0.5 m) of well-washed fluvioglacial sands. As expected, soils formed on sandy sediments exhibit lower productivity. According to various agrochemical parameters such as hydrolytic acidity, cation exchange capacity (CEC), and the content of mobile forms of K, Ca, Mg, and phosphorus (P), soils on sandy sediments significantly lag behind those formed on cover loams. The alteration in the composition of soil-forming rocks within the upper half-meter thickness is precisely responsible for the decrease observed in the upper 0–20 cm layer of the soil at sampling site 1–2.

Conversely, soils formed on the carbonate moraine deposits, cover loams (1–1, 2–1, and 2–2), gray forest soil, and typical chernozem exhibit

Table 3. Mineralogical composition of the clay fraction (<0.001 mm) of the studied soils.

Key area, #	**(1–1)**	**(1–2)**	**(2–1)**	**(2–2)**	**3**	**4**
The percentage of the mineral in the clay fraction (<0.001 mm), %:	—	—	—	—	—	—
Illite	41	29	35	39	44	43
Kaolinite + chlorite	32	51	50	33	34	38
Labile minerals	26*	18**	13**	26*	21***	18***
Quartz + feldspar	1	1	2	2	1	1
The percentage of the clay fraction of the mineral in the soil, %:	—	—	—	—	—	—
Illite	4.27	1.94	2.73	3.72	14.17	16.22
Kaolinite + chlorite	3.33	3.41	3.90	3.15	10.95	14.34
Labile minerals	2.71	1.20	1.01	2.48	6.76	6.79
Quartz + feldspar	0.10	0.07	0.16	0.19	0.32	0.38

Note: *Labile minerals are represented by smectite. **Labile minerals are represented by smectites and smectite packages in mixed-layer illite–smectite minerals. ***Labile minerals are represented by smectite and vermiculite.

consistently elevated values for the aforementioned indicators (refer to Tables 2–4). The granulometric composition of the examined soils ranged from sandy loamy sand to clay loam, as detailed in Table 2.

The findings from the analysis of the mineralogical composition of clay fractions (<0.001 mm) in the studied soils, presented in Figure 1 and Table 2, are illustrated through diffractograms. This table provides not only quantitative information on the relative content of fine minerals in the clay fraction of soils (<0.001 mm) but also includes data on the overall content of soil minerals in the respective soil samples. Figure 2 summarizes the results of our research, revealing the relationship between the soil properties and mobility of ^{137}Cs in the soil — plant continum.

Sod-podzolic sandy loam soil (1–1). The predominant components in the soil included dioctahedral illite (41%), a combination of kaolinite and chlorite (32%), with kaolinite being the prevalent component, and labile minerals represented primarily by smectite (27%). Additionally, a minor presence of chlorite and mixed-layer minerals, involving chlorite packets, was observed. The potential existence of vermiculite was noted. Quartz and feldspar were conclusively identified as components in the soil composition.

Sod-podzolic loamy sand soil (1–2). This soil type was characterized by a composition primarily composed of kaolinite (51%), dioctahedral illite (29%), and labile minerals (19%), such as smectites and mixed-layered illite-smectite minerals with smectite packages. The presence of vermiculite and a minor amount of chloride was conceivable. Additionally, quartz and feldspar were present.

Light-gray forest loam soil (2–1). The predominant components were dioctahedral illite (39%), kaolinite (34%), and labile minerals represented by smectite (27%). Illite was poorly crystallized, and quartz was definitively identified.

Light-gray forest sandy loam soil (2–2). The primary constituents of this soil type included kaolinite combined with chlorite (51%), well-crystallized dioctahedral illite (35%), and labile minerals represented by smectite (14%). Abundant minerals from the soil chlorite group were present, along with mixed-layer minerals involving chlorite packages. Quartz and feldspar were distinctly detected.

Gray forest clay loam soil (Greyzemic Phaeozem Albic) (3). This soil type featured dioctahedral illites (39–44%), kaolinite (34–36%), and labile minerals (22–25%) represented by smectite and vermiculite. Mixed-layer minerals with chlorite packages and a minor amount of chlorides were present. Quartz and feldspar were also part of the composition.

Table 4. Radioecological parameters of ecosystems at key areas.

Key area, #	**(1–1)**	**(1–2)**	**(2–1)**	**(2–2)**	**3**	**4**
Activity concentration of ^{137}Cs in the soil layer 0–20 cm, Bq kg^{-1}	144 ± 10	518 ± 56	266 ± 25	484 ± 24	20.2 ± 6.0	31.3 ± 8.5
The arial activity density of ^{137}Cs, kBq/m^2	28.8 ± 2.0	103.6 ± 11.2	53.3 ± 5.1	96.9 ± 4.8	4.04 ± 1.2	5.82 ± 0.24
Activity concentration of ^{137}Cs in the aboveground biomass of herbaceous pasture vegetation*, Bq kg^{-1} of air-dry mass	14.1 ± 2.2	82 ± 16	33.7 ± 1.8	24.9 ± 3.0	1.2 ± 0.9	1.3 ± 0.5
Aggregated transfer factor (T_{ag}) ^{137}Cs, (Bq kg^{-1} of plant)(/Bq/m^2 of soil area), $n \times 10^{-4}$	4.90 ± 0.84	7.92 ± 1.77	6.32 ± 0.69	2.57 ± 0.33	2.97 ± 2.40	2.23 ± 0.86

Note: *Pasture herbaceous vegetation was represented mainly (or only) by grasses (*Gramineae*).

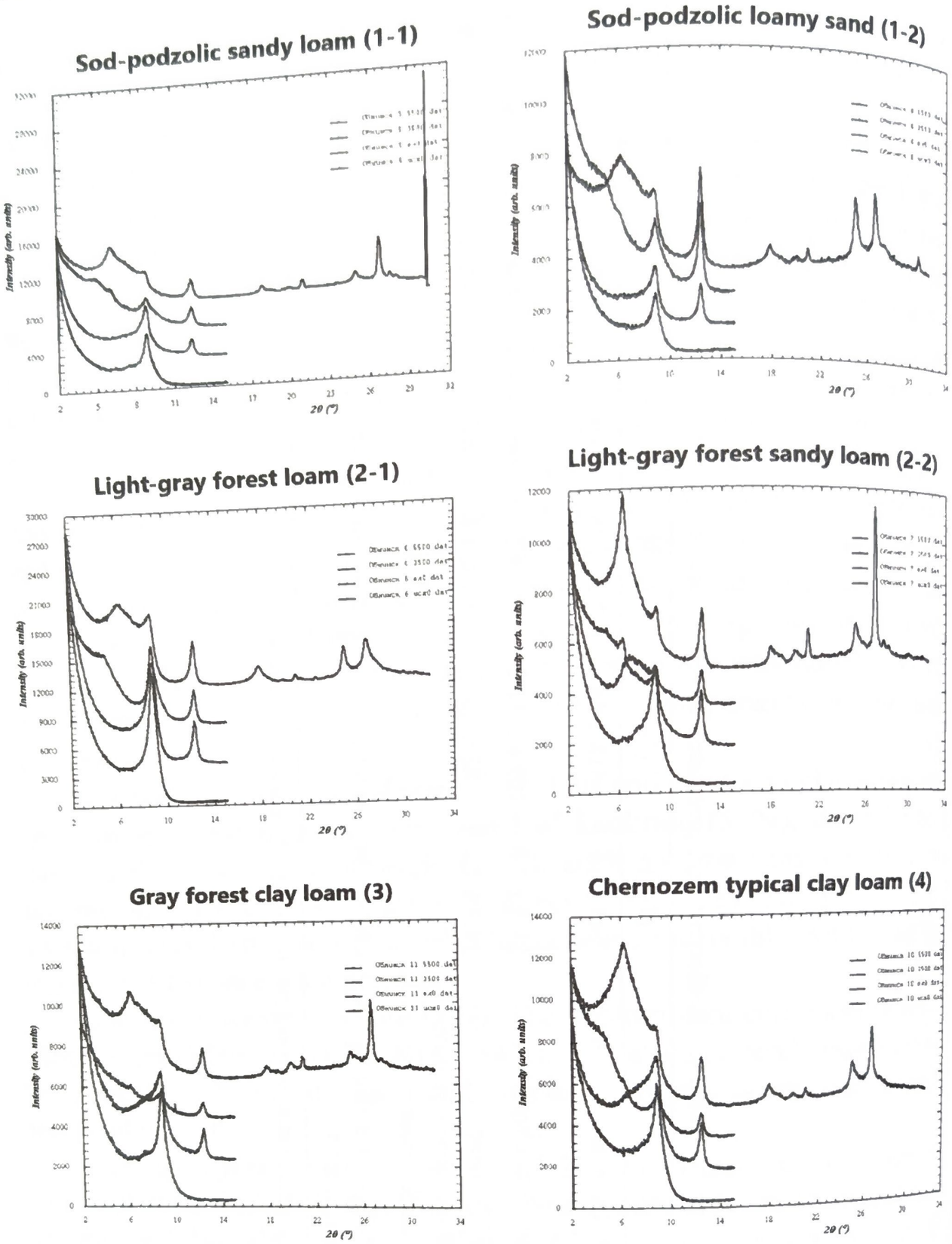

Figure 1. X-ray diffractograms of samples of the clay fraction extracted from: sod-podzolic sandy loam soil (1–1); sod-podzolic loamy sand soil (1–2); light-gray forest loam soil (2–1); light-gray forest sandy loam soil (2–2); gray forest clay loam soil (3); and chernozem typical clay loam (4), prepared for mineralogical analysis by the method developed by E. A. Kornblum.

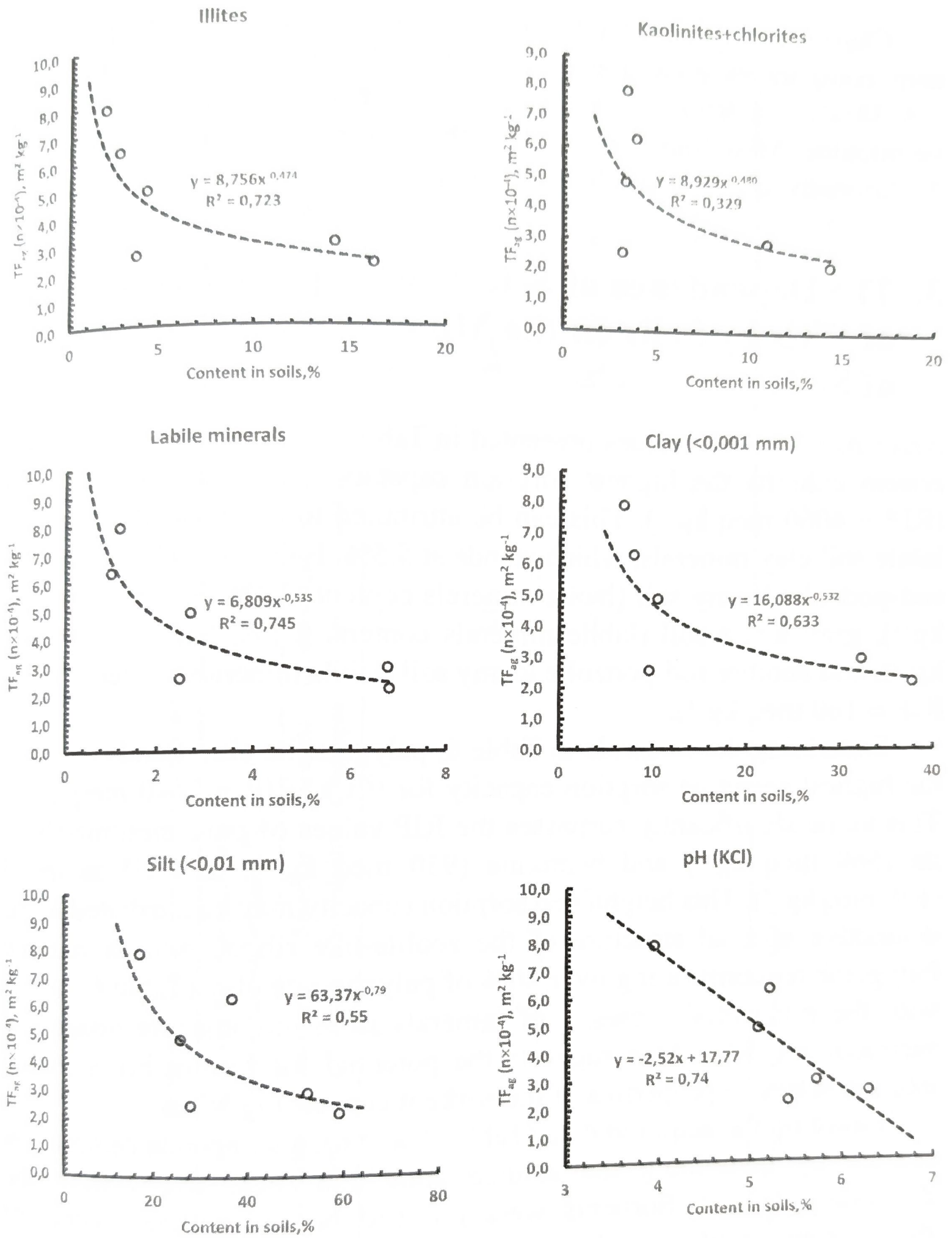

Figure 2. Dependence of the ^{137}Cs transfer to the aboveground biomass of pasture grasses and cereals on the mineralogical and granulometric composition of soils.

Chernozem typical clay loam (Haplic Chernozem*)* (4). The predominant components consisted of dioctahedral illites (32–43%), kaolinite (34–38%), and labile minerals (19–31%) represented by smectite and vermiculite. Mixed-layer minerals with chlorite packages were observed. Additionally, quartz and feldspar were present.

3. The Dependence of Selective Sorption Parameters of ^{137}Cs by Soils on the Mineralogical Composition of Soils

Analysis of the RIP values presented in Table 5 reveals that typical chernozem exhibits the highest sorption capacity among the studied soils (RIP = 4060 meq kg^{-1}). This can be attributed to its elevated content of labile soil clay minerals, which stands at 5.5%. Following closely are the sod-podzolic loamy soil (labile minerals content: 3.4%, RIP = 1400 meq kg^{-1}), gray forest soil (labile minerals content: 2.1%, RIP = 1270 meq kg^{-1}), and another sod-podzolic loamy soil (labile minerals content: 0.4%, RIP = 160 meq kg^{-1}).

Examining the minerals in Table 6, palygorskite clay stands out with the highest selective sorption capacity for ^{137}Cs (RIP = 2640 meq kg^{-1}). This value significantly surpasses the RIP values of pure montmorillonite (560 meq kg^{-1}) and bentonite (930 meq kg^{-1}), as well as trepel (630 meq kg^{-1}). This heightened sorption capacity may be attributed to the distinctive internal structure of the zeolite-like ribbon silicate mineral Palygorskite, constituting over 40% of palygorskite clay (Table 6), along with the substantial presence of minerals from the smectite group and vermiculite (39%). This suggests the potential for further investigation into the selective properties of the sorbent concerning ^{137}Cs.

Based on the acquired data (Tables 5 and 6), a composite sample was created by combining the studied soils and rock: trepel from the Zikeevsky deposit. Sorbents were grouped based on "the content of the same groups of minerals." Consequently, montmorillonite and bentonite were excluded from this sample. Palygorskite clay was omitted due to the high content of the mineral palygorskite with unknown sorption characteristics regarding ^{137}Cs, which were absent in other studied sorbents.

The composite sample underwent linear regression analysis, where the contents of individual minerals in the sorbent served as independent variables, and the RIP value was the dependent variable. The resultant dependencies are depicted in Figure 3.

Table 5. The mineralogical composition of soils under study.*

Soil	Content of soil fraction <0.001 mm, %	Mineralogical composition of soil fraction <0.001 mm, %				Minerals content in a bulk of soils, %				$RIP^{FES(Cs/K)**}$, meq kg^{-1}
		Dioctahedral Ilite	Kaolinite + Chlorite	Smectite + Vermiculite	Quartz + Feldspar	Dioctahedral Ilite	Kaolinite + Chlorite	Smectite + Vermiculite	Quartz + Feldspar	
Sod-podzolic soil, loamy sand	5.9	31	60	7	2	1.83	3.54	0.41	94.22	161
Sod-podzolic soil, silt loam	17.2	36	41	20	3	6.19	7.05	3.44	83.32	1397
Gray forest soil silt loam	10	44	34	21	1	4.40	3.40	2.10	90.10	1270
Chernozem typical	29	36	34	29	1	12.47	10.73	5.51	71.29	4056

Note: *Authors' unpublished data. **$Ag(TU)_n$ — masking agent.

Table 6. The mineralogical composition of mineral sorbents under study, %.

Mineral sorbent	Mineralogical composition of sorbent, %						$RIP^{FES(Cs/K)}$**, meq kg^{-1}
	Palygorskite	**Dioctahedral Ilite**	**Kaolinite + Chlorite**	**Smectite + Vermiculite**	**Quartz + Feldspar**	**Mica (Muscovite)**	
Palygorskite clay (Kaluga mineral deposit)*	42	6	—	39	7	—	2,642
Tripolite (Kaluga mineral deposit)	—	—	—	1.9	84.5	3	628
Bentonite (CAS: 1302-78-9)	—	—	5	85	6	4	929
Montmorillonite	—	—	—	100	—	—	559

Note: *The crystal chemical formula of Palygorskite is as follows: $Si_8Mg_5O_{20} \times (OH)_2(OH)_4 \times nH_2O$, where $n = 4$. **$Ag(TU)_n$ — *masking agent.*

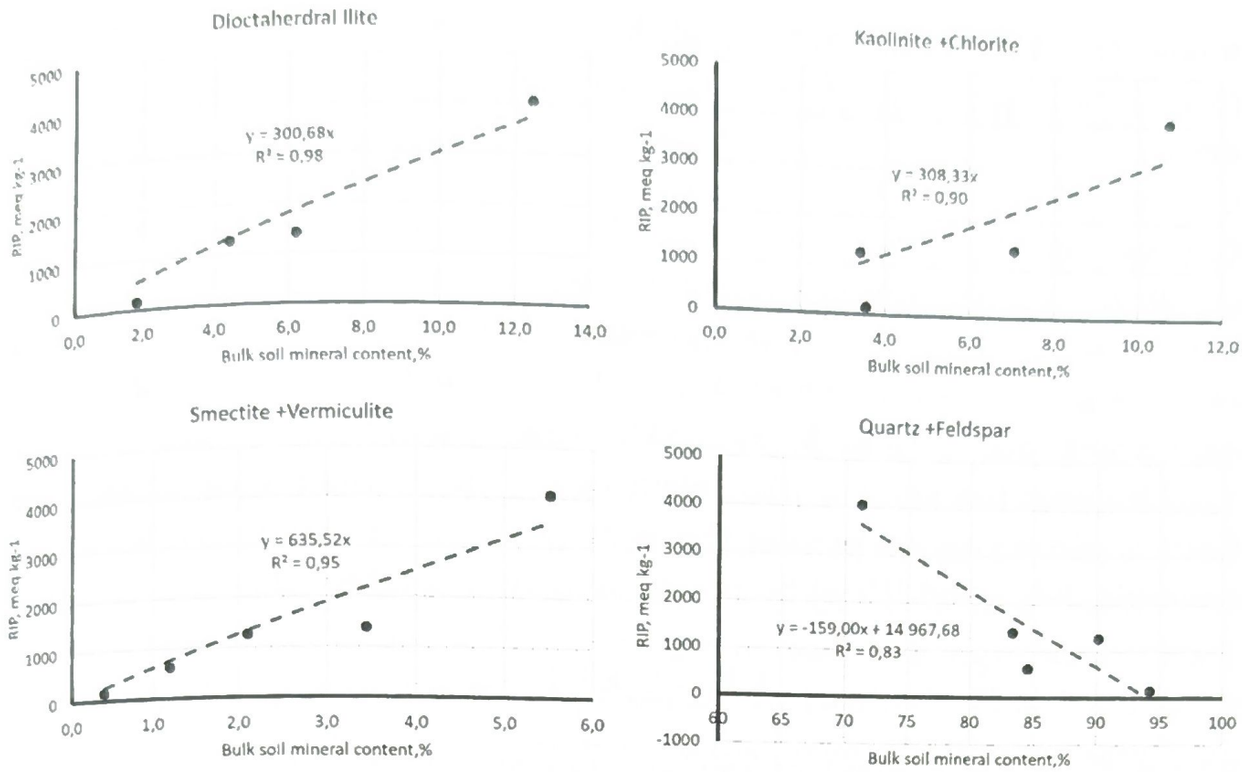

Figure 3. Dependence of the *RIP* value of the studied mineral sorbents (soils and tripoli) on the content of soil minerals.

The data obtained highlight a very high positive correlation between the content of *Dioctahedral Illite, Smectite + Vermiculite* mineral groups in the silty fraction of the studied soils and rocks and the $RIP^{FES(Cs/K)}$ value (meq kg^{-1}). Furthermore, a high positive correlation was observed between the content of the *Kaolinite + Chlorite* mineral group in the silty fraction and $RIP^{FES(Cs/K)}$. Conversely, a negative correlation was identified between the *Quartz + Feldspar* mineral group and $RIP^{FES(Cs/K)}$.

4. Effect of Selective Sorption Parameters of ^{137}Cs by Soils on Radionuclide Mobility in Soil–Plant System: Theoretical Aspects

In a broader context, understanding the RIP values (meq kg^{-1}) of soil enables the calculation of cesium K_d values (dm^3 kg^{-1}) under various ionic scenarios that naturally occur. This calculation is based on the expression (Cremers *et al.*, 1988; Smolders *et al.*, 1997)

$$K_d = \frac{\text{RIP}}{m_K + a \times m_{NH4} + b \times m_{Na}}, \quad (1)$$

where mx is the concentration of the corresponding ions in the solution (mmol dm^{-3}) and a and b are empirical constants accounting for the competitive effectiveness of Cs compared to K^+, NH_4^+, and Na^+ ions for specific sorption sites. Typically, it is assumed that $a = 5.3$ and $b = 0.02$ (Cremers *et al.*, 1988; Smolders *et al.*, 1997; Wauters *et al.*, 1996).

In natural conditions, two competing cations with ^{137}Cs typically considered are K^+ and NH_4^+. The influence of Na^+, Ca^{2+}, and Mg^{2+} cations is often negligible (Wauters *et al.*, 1994). In such cases, FES are nearly exclusively occupied by K^+ and NH_4^+ ions, resulting in $Z_{K,NH4} \rightarrow 1$.

Utilizing the value of the selective sorption potential of radiocesium RIP^{FES}, allows us to predict the accumulation of cesium isotopes (for example, ^{133}Cs and ^{137}Cs) by plants in natural conditions:

$$CR = f_{av} \times CF/K_d, \quad (2)$$

where f_{av} is the content of radiocesium available to plants in the soil, CR represents the (radio-)cesium concentration ratio, $(Bq\ kg^{-1})_{plants}/(Bq\ kg^{-1})_{soil}$, and CF denotes the (radio-)cesium concentration factor, $(Bq\ kg^{-1})_{plants}/(Bq\ dm^{-3})_{solution}$ (Wauters *et al.*, 1994).

It has been observed that CF is inversely proportional to the concentration of ions competing with radiocesium in the soil solution (Smolders and Shaw, 1995):

$$CF = k \times (1/([K] + [NH_4])), \quad (3)$$

where k is a proportionality coefficient dependent on plant characteristics.

Based on the theory of selective sorption of radiocesium, the following relationship holds:

$$K_d = RIP^{FES}/(([K] + K_c^{(NH4/K)} \times [NH_4]), \quad (4)$$

By combining Equations (3) and (4), expressions for predicting the accumulation of radiocesium in plants have been derived (Konoplev and Konopleva, 1999; Bulgakov and Shkuta, 2004):

$$CR = k \times f_{av} \times ([K] + K_c^{(NH4/K)} \times [NH_4])/(RIP^{FES}/([K] + [NH_4])). \quad (5)$$

Given that, for most soils and minerals, $K_c(NH_4/K)$ is approximately 5,

$$CR = k \times f_{av} \times ([K] + 5\ [NH_4])/(RIP^{FES}/([K] + [NH_4])). \quad (6)$$

5. Effect of Selective Sorption Parameters of ^{137}Cs by Soils on Radionuclide Mobility in Soil–Plant System: Data from Field Experiments

To investigate the impact of various countermeasures on alterations in the parameters of ^{137}Cs selective sorption in soil and its mobility within the soil–plant system, a field experiment with pasture grasses was conducted on meadow-boggy soil.

The results indicate that the implementation of agrotechnical and agrochemical protective measures influences the ^{137}Cs distribution coefficient (K_d) between the solid and liquid phases of the soil, as well as the potential for selective sorption of radiocesium. This is evident from the data presented in Table 7. Plowing emerges as a significant factor, increasing this parameter by approximately twofold. This increase is attributed to the mixing of the upper humus layer with the mineral horizon, thereby enhancing the soil's sorption capacity for ^{137}Cs. Lime and mineral fertilizers also impact K_d, albeit to a lesser extent, with the maximum increase observed in the variant with the addition of 4.5 t ha^{-1} of lime.

Agrotechnical measures, such as disking and plowing, similarly result in a twofold increase in the potential for selective soil sorption compared

Table 7. Correlation coefficients of T_{ag} ^{137}Cs in the grasses with the exchange form of ^{137}Cs, with K_d and RIP.

No.	T_{ag} ^{137}Cs, $n \times 10^{-4}$	RIP	K_d ^{137}Cs	NH_4OAc, %
1	93.4	166	87.2	4.0
2	37	348	185	2.05
3	30.1	232	119	1.01
4	20	265	139	1.02
5	18.9	273	126	3.11
6	17.6	298	159	1.66
7	19.6	364	194	1.26
8	18.5	315	168	2.06
9	8.4	381	199	0.74
		Correlation coefficient (*r*)		
Between 1–9 variants		−0.728	−0.673	0.741

Table 8. Comparative results of quantitative phase analysis of trepel and complex sorbent.

Sorbent	The mineral phase	%
Tripolite (Zikeyevskoye deposit, Kaluga region)	Mica structures (muscovite) $KAl_2[AlSi_3O_{10}](OH)_2$	3
	Montmorillonite $(1/2Ca)_{0.7}(Al,Mg,Fe)_4(Si,Al)_8 \times O_{20}(OH)_4 \times nH_2O$	1.9
	Quartz SiO_2	7
	Cristobalite SiO_2	77.5
Complex sorbent	Zeolite content $K_{9.72}(Al_{7.32}Si_{28.08}O_{72})(H_2O)_{25.5}$	50 ± 4
	Mica structures (muscovite) $KAl_2[AlSi_3O_{10}](OH)_2$	4
	Montmorillonite $Al_2[Si_4O_{10}](OH)_2 \times nH_2O$	15
	Quartz SiO_2	4
	X-ray amorphous phase	All the rest

to the control (Table 7). The highest RIP value was recorded in the variant with increased doses of mineral fertilizers and lime, combined with disking and plowing.

Despite a lack of correlation between the content of the ^{137}Cs exchangeable form (NH_4OAc, pH 7.0 extracted) and the ^{137}Cs distribution coefficient between the solid and liquid phases of the soil (Table 8), a close correlation was found between the T_{ag} (^{137}Cs) of the grasses and the content of the ^{137}Cs exchangeable form ($r = 0.741$). Additionally, negative correlations were established between T_{ag} (^{137}Cs) in the grasses and K_d ($r = -0.673$) and RIP ($r = -0.728$).

6. Investigation of Agromeliorants Application to Soil, Considering Their Impact on Biological Availability Based on RIP

The utilization of specialized sorbents presents a promising approach to mitigating the transfer of ^{137}Cs into crops in radioactively contaminated areas. These sorbents can be categorized as natural (clays and minerals, mainly of local origin) or synthetic.

The efficacy of this technique is contingent upon the choice of agromeliorant employed, such as zeolites, bentonites, tripoli, local palygorskite, and bentonite clays.

Research conducted in the post-Chernobyl period revealed that purposefully altering the sorption properties of sod-podzolic sandy and sandy-loam soils through the introduction of natural sorbents can reduce the transference of ^{137}Cs into crops by approximately five times. This reduction is attributed to the absorption of radionuclides in crystal structures, rendering them inaccessible for root uptake by plants.

Currently, significant emphasis is placed on sorbents whose industrial deposits are situated in contaminated areas or at distances conducive to cost-effective transportation to application sites. For instance, near the Chernobyl-affected territories in the Kaluga region, sizable deposits of natural minerals, such as the Zikeevskoe deposits of trepels and opokas and the Borshchevskoe deposit of palygorskite clays, exist. These deposits serve as potential ameliorants–sorbents for ^{137}Cs. When used judiciously, they have demonstrated effectiveness in reducing the transfer of ^{137}Cs from soil to crop products.

7. Development and Testing of a Synthetic Complex Sorbent Based on Tripolite to Reduce ^{137}Cs Mobility in the Soil–Agricultural Plants System

A complex sorbent (CS) was derived from trepel through chemical modification, involving treatment at $t = 150°C$, with a solution of aluminum hydroxocomplex ($K_3[A1(OH)_6]$) in 45% KOH. The process is followed by the neutralization of the resulting alkaline suspension with phosphoric acid, adjusting the pH to 7.0, and subsequent drying to achieve a humidity of approximately 1% (Patent for Invention No. 2336257, dated 10.20.2008).

The obtained CS is a composite of permutite, synthesized through a hydrothermal method ($Na_2O{\cdot}Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$), and amorphous silica (silica gel), SiO_2 (Table 9).

The primary raw material for this CS is trepel, sourced from the Zikeevsky deposit in the Kaluga region. In terms of specific surface area and sorption capacity, this CS matches trepel, yet surpasses it in Ba^{2+} absorption capacity by 4–5 times and exhibits a highly selective capacity for Cs^+ ions at FES-sites that is 65 times greater than that of trepel (Table 10).

With its substantial specific surface area, this sorbent also proves versatile for the absorption of harmful volatile substances such as ammonia, acid vapors, and organic solvents.

Table 9. Values of specific surface area and absorption capacity of natural and synthetic complex sorbent.

Sorbent	CEC, cmol(+) kg^{-1}		FES, meq кг$^{-1}$	Specific surface area by N_2, m^2 g^{-1}	
	Mean	Standard error	Mean	Mean	Standard error
Montmorillonite untreated, FLUKA, Cat. No 69911	52.30	2.43	70.9	—	—
Bentonite, Riedel-deHaën, Cat. No 18609	52.10	2.44	—	62.3	1.9
Tripolite (Kaluga region)	20.67	1.29	17.1	89.5	2.7
Palygorskite (Kaluga region)	24.52	0.32	—	—	—
Complex sorbent	105.5	5.5	1,111	130.3	3.9
Gray forest soil (Kaluga region)	16.27	0.13	25.1	—	—

Table 10. Aggregated indicators of selective sorption of ^{137}Cs by soils and complex sorbent modification CS-20CX.

Variant	K_d, ^{137}Cs, dm^3 kg^{-1}	RIP, meq kg^{-1}
Soil–Control	150 ± 13	1,550 ± 140
Soil + NPK	135 ± 55	1,400 ± 570
Soil + SUPRODIT 1.36 g kg^{-1}	172 ± 4.4	1,770 ± 50
CS-20CX	1,320 ± 210	13,600 ± 2,200

8. Development and Testing of Organic–Mineral Fertilizer "SUPRODIT" to Reduce ^{137}Cs Mobility in the Soil–Agricultural Plants System

The innovative complex fertilizer developed was named "SUPRODIT." It constitutes a mechanical mixture (50%/50%, m/m) of the CS and modified peat with elevated levels of potassium humates and nitrates.

The elemental composition of the complex fertilizer is as follows:

N (total nitrogen): 21.96%,
P_2O_5: 15.73%,
K_2O: 11.20%,
SiO_2: 12.54%,
Al_2O_3: 1.65%,
CaO: 1.92%,
MgO: 0.30%,
Fe_2O_3: 0.96%, and
MnO_2: 0.14%.

Approximately 33.60% of the mass constitutes organic matter.

The molar ratio of SiO_2/Al_2O_3 is 12.90.

The CEC of the complex fertilizer is 126 ± 2 meq per 100 g, which is six times higher than that of the initial material, tripolite.

To assess the effective dose of sorbent application for reducing the migration ability of ^{137}Cs, the well-established principle of additivity is employed. This principle states that the desired value of $RIP_{(sorbent+soil)}$ for the reclaimed mixture (soil + sorbent) is a linear superposition of the $RIP_{sorbent}$ and RIP_{soil} values, each multiplied by the mass fraction (N_m) of its component in the mixture, according to the formula

$$\mathbf{RIP}_{\text{sorbent+soil}} = (\mathbf{RIP}_{\text{sorbent}} \times N_{m,\text{sorbent}} + \mathbf{RIP}_{\text{soil}} \times N_{m,\text{soil}})/(N_{m,\text{sorbent}} + N_{m,\text{soil}}) \quad (7)$$

It is assumed that there is no interaction among the components.

During the vegetation experiment conducted at the NRC of Kurchatov Institute — RIRAE premises, the impact of "SUPRODIT" on wheat productivity (*Enita* variety) and the uptake of ^{137}Cs from sod-podzolic loam soil by plants was studied in comparison with industrial fertilizers (NPK and Nitrophoska). The fertilizers were applied before the experiment at a rate of 0.15 g kg^{-1} of soil for N, P_2O_5, and K_2O in the form of NH_4NO_3, KH_2PO_4, and K_2SO_4 solutions, respectively. The dose of Nitrophoska was calculated based on the content of N, P_2O_5, and K_2O in the NPK variant. Nitrophoska contains 10% of each element. The "SUPRODIT" dose was calculated based on the K_2O content in the NPK variant (1.63 g kg^{-1}). Additionally, ^{137}Cs was introduced at a rate of 100 kBq kg^{-1}.

As indicated in Table 11, the application of "SUPRODIT" to the soil results in a significant increase (by 15%) in both the soil K_d and RIP values.

Table 11. Influence of the SUPRODIT on wheat productivity and accumulation of ^{137}Cs in grain on sod-podzolic soil (RIRAE vegetation experiment).

Variant	Grain mass, g vessel^{-1}	CR ^{137}Cs, $n \times 10^{-2}$
NPK + ^{137}Cs	12.0 ± 0.4	3.8 ± 0.6
SUPRODIT + ^{137}Cs	13.1 ± 0.4	1.5 ± 0.4
Nitrophoska + ^{137}Cs	11.5 ± 0.3	2.7 ± 0.2

9. Conclusion

The results obtained clearly show how the granulometric and mineralogical composition of soils directly impacts the mobility of ^{137}Cs in the soil–plant system. There is a confirmed negative correlation between the illite content and labile minerals (primarily from the smectite group) in soils and the aggregated transfer factors of ^{137}Cs in plants. The content of the clay fraction in soils has also been discovered to have a negative correlation with the aggregated transfer factors of ^{137}Cs in plants. The soil's granulometric and mineralogical composition plays a crucial role in influencing the ^{137}Cs interception potential (RIP) and the bioavailability and mobility of this radionuclide.

The identified dependencies offer solid scientific reasoning for choosing both natural and synthetic sorbents with a strong potential for selective sorption, effectively aiding in the remediation of contaminated areas.

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