Content of radionuclides (^{226}Ra, ^{232}Th, ^{40}K, ^{137}Cs) in soils of the North-West region of Russia formed on three types of soil forming rocks

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Abstract. The results of a study of the content of natural radionuclides (NR) (^{226}Ra, ^{232}Th, ^{40}K) and technogenic ^{137}Cs in soil samples formed on the most common types of soil-forming rocks of the North-West: lake-glacial (non-boulder and tape clay), glacial and water-glacial deposits are presented. Soil sections laid in the Pskov, Novgorod and Leningrad regions. The granulometric composition in the upper part of the soil profile is lighter than in the parent rock. This is reflected in the NR content in the profile of these soils: with a decrease in the fractions of physical clay and silt, the content of ^{226}Ra, ^{232}Th and ^{40}K decreases. This is due to the fixation of natural radionuclides by secondary clay minerals. According to the increase in the average specific activity of all NRs, the soils form the following sequence: soils on water-glacial deposits - soils on moraines - soils on lake-glacial deposits. A comparison of the average specific activity of natural radionuclides and their ranges in the upper part of the soil (0-5, 5-10 and 10-20 cm) and in the parent rock (90-100 cm) revealed a higher content of radionuclides in parent rocks (lake-glacial and moraine deposits). In the soils on water-glacial deposits, no significant difference was found.

1 Introduction

One of the most pressing environmental problems is the radiation pollution of ecosystems. Regardless of the pollution source, its effects are always reflected in soils. At present, significant factual material has been accumulated on the radioactive contamination of soils in Russia. However, it is either strongly averaged as is the case with the data presented in Sources and Effects of Ionizing Radiation (^{226}Ra - average specific activity of 35 ± 4 Bq/kg, with a typical range of 17-60 Bq/kg; ^{232}Th - 30 ± 3 Bq/kg , 11-64 Bq/kg; ^{40}K - 400 ± 24 Bq/kg, 140-850 Bq/kg), or applies only to soils that have been contaminated with technogenic radionuclides at different times [1, 2].

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An extensive collection of soil monoliths (SM) and samples from various regions of Russia, selected from 1904 to the present and stored in the Dokuchaeva Central Soil Science Museum (Museum) gives an unique opportunity to study the content of radionuclides in soils and parent rocks. The aim of the work is to study the content of natural radionuclides 226Ra, 232Th, 40K and technogenic 137Cs in soils formed on the three prevailing types of parent rocks.

2 Materials and methods

The objects were soil samples of different selection periods from 11 PM and 6 sections, selected from 1926 to 2017 and included in the Bioresource collection of soil monoliths of the Museum. The soil monolith is a volumetric prism of undisturbed soil with standard dimensions of 100x20x5 cm. Samples from SM and sections were taken in layers from depths of 0-5, 5-10, 10-20 and 90-100 cm. Sample preparation and subsequent analysis of the samples were carried out in the same way and by generally accepted methods. All soils are formed on parent rocks (PR), the most common in the North-West (Leningrad, Novgorod and Pskov regions). These are lake-glacial, glacial and water-glacial deposits.

The soils of the Tikhvin, Boksitogorsky and Tosnensky districts in the Leningrad region were investigated. The studied soils belong to 6 taxonomic types [3]: Entic Podzol (section 1), Rubic Arenosol (section 1567), Gleysol (sections 2116), Haplic Stagnosols (sections 1560 and 711), Histicgleyisol (section 261) and Haplic Albeluvisol (section MLK-4). Two soils are included in the Red Book of Soils of the Leningrad Region and belong to the categories of “Soil Standards” (section 711) and “Soils - Monitoring Objects” (section 261) [4]. The Novgorod region (Novgorod and Valdai districts) is represented by: Umbric Albeluvisol (section 414), Haplic Cambisol (section ENVM-10), Histosol (section 3.29), Gleysol (section 10.17), Rubic Arenosol (sections 50, 7.17) Soils were studied in the Pskov region: Stagnic Albeluvisol (section 287), Entic Podzol (section 2138) and Haplic Albeluvisol (sections 383 and 3.17) from Novosokolnichesky and Kuninsky districts.

Lake-glacial sediments (6 soils studied) are characterized by a heavy granulometric composition and are represented by well-sorted material (non-boulder clay), or material with a thin layering (tape clay), due to the seasonal formation of deposits [5]. Moraines (7 soils) are heterogeneous in mineralogical-petrographic and particle size distribution. Water-glacial (4 soils) are characterized by sandy granulometric composition [5].

It is known that the behavior of radionuclides in soil depends on many factors: the genetic characteristics of the soil, its regimes (water, acid, redox), the content of organic matter in the soil, and particle size, chemical and mineralogical compositions of the soil [3, 6-9], as well as from the hydrophysical properties of the soil [10-14]. pHн2o and particle size distribution to the greatest extent, affecting the behavior of radionuclides in soils [15, 16], were determined in the samples. The specific activity (RA) of radionuclides (226Ra, 232Th, 40K, 137Cs) in the samples was determined by gamma spectrometry at the All-Russian Research Institute of Radiology and Agroecology [1].

Statistical processing of the obtained data was carried out by the method of descriptive statistics: arithmetic mean (M), standard deviation (σ), Mann-Whitney U-test and coefficient of variation (Vσ) [2]. Vσ was calculated for the entire set of samples, as well as for sampling layers separately for PR groups. Based on the literature data and statistical processing of the obtained material, Vσ exceeding 30% was adopted as an indicator of the heterogeneity of RA NR [15].

3 Results and discussion

The content of physical clay (fractions less than 0.01 mm) in soils on lake-glacial sediments (hereinafter referred to as group I) averages 56 ± 18.3%, and the fraction of silt (fractions less than 0.001 mm): 16.0 ± 8.2% (Table 1). It is characteristic that there is the content of physical clay and silt in the soils on lake-glacial sediments in the upper part of the profile (0-5, 5-10 and 10-20 cm) which is one and a half to two times less than in parent rocks, except for soil of a sect. 2116, where the difference is not significant.

Table 1. Granulometric composition and reaction of the medium in the studied soils.

Objects of study (sampling depth)	pH range of aqueous suspension	Range of fraction content,%	
		<0,001 mm	<0,01 mm
Soils on lake-glacial deposits (0-20 cm)	4.1 – 6.0	5.0 – 35.0	28.0 – 82.0
Lacustrine-glacialdeposits (90-100 cm)	6.1 – 7.9	16.0 – 46.0	69.0 – 94.0
Lacustrine-glacialdeposits (90-100 cm)	3.7 – 6.6	12.2 – 48.9	4.0 – 25.7
Morainedeposits (90-100 cm)	5.1 – 8.3	8.1 – 73.4	14.0 – 26.3
Soils on water-glacial deposits (0-20 cm)	4.6 – 5.7	4.2 – 45.9	9.2 – 50.1
Water-glacialdeposits (90-100 cm)	5.3 – 5.9	1.3 – 14.5	3.5 – 24.2

Compared to soils group I, the average content of silt fraction in soils (over the entire profile) on moraines (group II) is less (11.4 ± 8.6%), while the content of the fraction of physical clay is almost half (29.6 ± 17.1%). The difference in the content of physical clay and silt in the upper part of soils and PR (moraine) is insignificant (does not exceed 6.5%), with the exception of 2 sections. In sect. 414, the difference in the content of fractions is 15–20% with the largest number of them in the rock, and in sect. 383, the content of fractions of physical clay and silt at a depth of 90-100 cm almost doubles compared with the upper 0-20 cm (73.4 and 26.3%, respectively).

Soils on water-glacial deposits (group III) have a light particle size distribution - from loose sand to light loam. The content of physical clay and silt in soils averages 19.7 ± 14.8% and 16.9 ± 14.2%, respectively. In PR, the amount of these fractions decreases by two to three times. In soils on water-glacial sediments, in comparison with soils of groups I and II, the largest number of sand fractions is recorded (96 and 93% in sections 7.17 and 1, respectively). This indicates the predominance of primary minerals in the soils of group III. Differences in the content of primary and secondary (finely dispersed fractions) minerals can affect RA NR [15, 17, 18].

It is known that the behavior of radionuclides is associated with soil acidity. Thus, according to the literature, the strongest sorption of thorium-232 is observed in soils with neutral and slightly alkaline environmental reactions, and the smallest in acidic [17]. Soils of the groups I and II in the upper part of the profile in most cases have an acidic reaction of the medium (Table 1), and only in three soils (sections 711, 10.17 and 3.17) the reaction is close to neutral. The reaction of the medium in the PR samples of these groups varies in a wide range - from weakly acidic to slightly alkaline. This is probably due to the presence in some samples of primary minerals containing carbonates. Soils on water-glacial sediments along the entire profile have an acid reaction of the environment.

3.1 The content of radionuclides

Radium-226 is present in the nature in a dispersed state and practically does not form part of individual minerals. Radium-226 in the soils has the greatest migratory ability. Its maximum sorption was noted in soils with a high content of silt fraction. Up to 40% of all compounds with 226Ra in soils are in water-soluble, metabolic, and acid-soluble forms [9, 18]. The specific activity (RA) 226Ra in all soils varies over a wide range from 3.8 to 50.0 Bq/kg (M 20.5 ± 10.4 Bq/kg) (Table 2). It should be noted that in organogenic horizons the specific activity is lower than the sensitivity of the device. The widest range of RA element is typical for soils on moraine deposits, and the narrowest - for soils on lake-glacial. In PR samples, RA 226Ra varies in a narrower range of 5.1 - 50.0 Bq/kg (M 22.7 ± 11.7 Bq/kg).

The difference in the average values of the specific activity of the radionuclide, taking into account the standard deviation (σ) in the samples from the upper part of the profile (0-5, 5-10, 10-20 cm), as well as in the PR is not significant. In general, the average values of Radium-226 at a depth of 90-100 cm are higher than in the upper part of the profile, with the exception of soils on water-glacial deposits, where the situation is opposite.

The differences between the values of RA 226Ra in soils on lake-glacial, moraine and water-glacial deposits according to the Mann-Whitney criterion is significant only between I and III, as well as II and III groups. This is due to lower values of specific activity in soils on water-glacial deposits compared with soils formed on other types of PR.

An analysis of the values of the coefficient of variation (Vσ) by groups revealed that the values of Vσ (heterogeneity) in the soils exceed 30% of the threshold and increase in the order: lake-glacial, glacial and water-glacial deposits. According to the individual depths from which the samples were taken, Vσ also exceeded 30%, with the exception of depths of 5-10 and 90-100 cm in the soils of group I. The greatest heterogeneity was noted in soil samples of group III at a depth of 10-20 cm in the illuvial-glandular and glandular-metamorphic horizons.

Table 2. The results of statistical processing of the content of natural radionuclides

Objects of study (sampling depth)	Radio-nuclide	Number of samples (N)	Mean value (M) and standard deviation (σ)	Specific Activity Range (R_A)	Coefficient of Variations (Vσ)
		Unit	Bq/kg		%
Soils on lake-glacial deposits (0-20 cm)	^{226}Ra	18	22.0±9.6	12.0 – 39.4	43.7
	^{232}Th		30.6±13.0	12.2 – 49.2	42.5
	^{40}K		606±236	302 – 903	39.0
Lake-glacial deposits (90-100 cm)	^{226}Ra	6	26.9±7.0	22.0 – 35.6	25.9
	^{232}Th		51.7±9.3	37.0 – 60.8	18.0
	^{40}K		868±235	470 - 1043	27.1
Soils on moraines (0-20 cm)	^{226}Ra	21	21.0±8.8	7.0 – 43.0	41.8
	^{232}Th		25.8±11.2	10.0 – 45.0	43.6
	^{40}K		614±257	50 – 890	41.8
Moraine deposits (90-100 cm)	^{226}Ra	7	26.0±13.1	14.5 – 50.0	50.4
	^{232}Th		34.5±9.7	25.0 – 48.5	28.1
	^{40}K		698±160	417 - 890	23.0
Soils on water-glacial deposits (0-20 cm)	^{226}Ra	12	13.7±9.7	3.8 – 39.7	71.0
	^{232}Th		18.3±7.4	12.5 – 36.0	40.4
	^{40}K		466±110	378 – 740	23.7
Water-glacial deposits (90-100 cm)	^{226}Ra	4	10.7±5.3	5.1 – 16.6	49.9
	^{232}Th		17.0±9.2	11.3 – 31.7	53.8
	^{40}K		441±76	384 - 557	17.1

Thorium 232. The average content of 232Th in the soils of the USSR was 31.1 Bq/kg (0.24 to 400 Bq/kg). Up to 10% of all compounds with 232Th in soils are in water-soluble, exchange, and acid-soluble forms, and the number of compounds strongly bonded and bound to sesquioxides reaches 80% [18]. RA 232Th in all soils varies between 10.0 - 60.8 Bq/kg (M 28.7 ± 14.1 Bq/kg) and is determined by the radionuclide content in parent rocks (M 36.5 ± 16.2 Bq/kg) (Table 2). As in the case of 226Ra, in almost all organogenic horizons the specific activity is lower than the sensitivity of the device. The widest range of

RA 232Th is characteristic of the upper part of soils of groups I and II. The difference in the average values of the specific activity of the radionuclide taking into account σ in the samples from the upper part of the profile, as well as in PR, is significant only for soils of group I. There is a tendency to a higher Thorium-232 content at a depth of 90-100 cm compared to the upper part of the profile, with the exception of soils on water-glacial deposits, where the situation is the opposite, although the difference between the average values is only 1.3 Bq/kg.

The calculation of the Mann-Whitney U-criteria showed differences in the 232Th content in the same pairs (groups I and III, and II and III) as for Radium-226. The Vσ calculated for the groups is 40.5–43.5% and increases in the series: glacial, lake-glacial and water-glacial deposits. In terms of the individual depths from which the samples were taken, Vσalso exceeded 30%, with the exception of samples of parent rocks of the first and second groups, as well as for samples from a depth of 5-10 cm in soils on water-ice deposits.

Potassium-40 is one of the main (in activity) natural radionuclides in soils and plants. In soil, its specific activity can be 300-1000 Bq/kg. During the decay, Potassium-40 turns into a stable 40Ca. The main K-containing minerals are biotite, muscovite, orthoclase and illite [9, 18].

The content of 40K in soils is 50 - 1043 Bq/kg (M 606 ± 236 Bq/kg) (Table 2). As in the case of Radium-226 and Thorium-232, in some organogenic horizons its specific activity is lower than the sensitivity of the device. The presence of a radionuclide in some organogenic horizons is probably associated with an insignificant admixture of mineral particles in them. The widest range of RA 40K is typical for the soils of the second group, and the narrowest for the third. In PR samples, the specific Potassium-40 activity varies in a narrower range of 384–1043 Bq/kg (M 698 ± 238 Bq/kg).

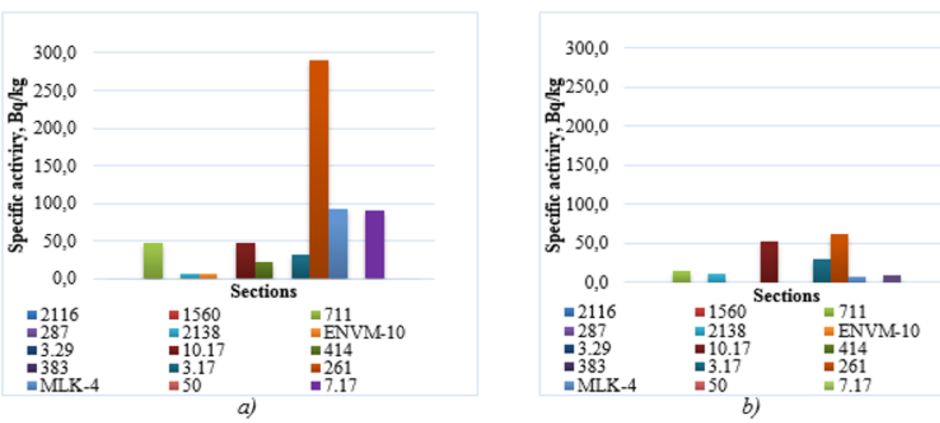

Fig. 1. The specific activity of ^{137}Cs in the studied soils at depths: *a*) 0-5 cm and *b*) 5-10 cm.

The difference between the upper part of the profile and the parent rock, as well as the tendency to a higher 40K content in PR samples, are of the same nature as in the case of Thorium-232. The calculation of the Mann-Whitney test revealed the same patterns between the three groups as for Radium-226 Thorium-232. The coefficient of variation Vσ in comparison with other NRs has low values. Thus, in soils on lake-glacial and moraine deposits, it amounted to 38.8 and 37.2%, respectively, and in soils on water-glacial deposits - 23%. The individual depths from which the samples were taken showed a tendency to a decrease in Vσ with depth, with the exception of group III samples at a depth of 90-100 cm, in which the coefficient is slightly higher than in layers of 5-10 and 10-20 cm. It should be noted that in soils on water-glacial deposits, the coefficient of variation in depth does not exceed 33.5%.

Cesium-137 is one of the main long-lived technogenic radionuclides (half-life = 30.17 years). Cesium-137 is a chemical analogue of a biologically important element of potassium [19]. The artificial 137Cs radionuclide was found only in the upper part of the profile (0–20 cm) of eight modern soils selected after 1996 (sect. 711, 2138, ENVM-10, 10.17, 3.17, 261, MLK-4, 7.17) and 1971 soil year of selection (sect. 414) (Fig. 1). The presence of cesium-137 in sect. 414 may be related to local pollution. The radionuclide content in soils varies between 6.7 - 290 Bq / kg (M 48.9 ± 65.3 Bq/kg) with the largest amount in the soils of the Leningrad (section 261 - 290 Bq/kg and MLK-4 - 93.6 Bq/kg) and Novgorod region (p. 7.17 - 90.9 Bq/kg). The bulk of cesium-137 is observed in the upper 0-5 cm, below its content decreases sharply. An exception is soil samples of sect. 10.17, where the largest amount of radionuclide was noted at a depth of 5-10 cm. This may be due to soil mixing during land reclamation.

4 Conclusion

The specific activity of NRs in the studied soils differs from the data presented in the report “Sources and effects of ionizing Radiation”, both for the entire population of soils and taking into account PR [1]. Soils on water-glacial deposits differ most strongly, the RA indices for Radiation-226 and Thorium-232 in which are slightly lower than in [1] (226Ra - 35 ± 4 Bq/kg; Th - 30 ± 3 Bq/kg). Comparison of the average specific activity of natural radionuclides and their ranges in the upper part of the soil (0-20 cm) and in parent rock (90-100 cm) revealed a higher content of radionuclides in parent rocks (lake-glacial and moraine deposits). In the group of soils on water-glacial deposits, no significant difference was revealed.

According to the increase in the average specific activity of all NRs, the soils form the following sequence: soils on water-glacial deposits - soils on moraines - soils on lake-glacial deposits.

The content of NRs in 3 types of the main PR of the North-West was revealed:

- Lake-glacial deposits: 226Ra: 26.9 ± 9.2 (22.0 - 35.6) Bq/kg;
232Th: 51.7 ± 9.3 (37.0 - 60.8) Bq / kg;
40K: 868 ± 236 (470 - 1043) Bq/kg.
- Glacial (moraine) deposits: 226Ra: 26.0 ± 13.1 (14.5 - 50.0) Bq/kg;
232Th: 34.5 ± 9.7 (25.0 - 48.5) Bq/kg;
40K: 698 ± 160 (630 - 890) Bq/kg.
- Water-glacial deposits: 226Ra: 10.7 ± 5.3 (22.0 - 35.6) Bq/kg;
232Th: 17.0 ± 9.2 (37.0 - 60.8) Bq/kg;
40K: 441 ± 75.6 (470 - 1043) Bq/kg.

Technogenic 137Cs was found in modern soil samples (1996-2017 selection), as well as in the 1971 sample (sect. 414). Its RA varies between 6.7 - 290 Bq/kg (48.9 ± 65.3 Bq/kg), with the highest content in the soils of the Leningrad and Novgorod regions.

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