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DEGRADATION, REHABILITATION, AND CONSERVATION OF SOILS

Speciation of Radium-226 in Podzols of Northeastern Sakhalin in the Impact Zone of the Oil Field

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Abstract—Podzols in oil-mining areas of northeastern Sakhalin were examined. The physicochemical properties of the podzols on the industrial plot, on the adjacent territory, and in the background landscapes were characterized. It was found that the distribution of the particular forms of radium-226 in the podzols contaminated with slightly saline and slightly radioactive stratal water differs from that in the background soils. In the contaminated podzols, the portion of exchangeable radium-226 increases in the lower part of the profile; the accumulation of mobile water-soluble and acid-soluble radionuclid increases in the illuvial horizons and decreases in the upper organic horizons.

Keywords: natural radionuclides, migration, accumulation, soil, pollution, physicochemical properties

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INTRODUCTION

Natural radionuclides extracted by humans from the deep earth layers have become important pollutants of the environment. Their considerable input takes place in the areas of petroleum production, storage, and transportation. In such places, the environment and the personnel of industrial enterprises, as well as the local population, are subjected to ionizing radiation [5].

Stratal water is the main source of radioactive isotopes in oil-mining areas. This water contains large amounts of soluble inorganic compounds of sulfates and chlorides. There are also many alkali-earth elements, including radioactive radium. The total concentration of dissolved solids in stratal water varies from 5 to 300 g/L [25]. The radioactivity of stratal water mainly depends on the concentration of radium-226 (from the decay chain of uranium-238) and radium-228 (from the decay chain of thorium-232). The concentration of radium isotopes in the stratal water may be two–three orders of magnitude higher than their background concentrations [20]. Soil contamination with stratal water may result in the formation of radioactively contaminated areas with further migration of radionuclides to the surface and ground waters, including drinking water [2].

All radium isotopes differ from other radionuclides by their high radiotoxicity. Radium-226 is one of the most toxic and widespread long-living alpha emitters. Its maximum permissible concentration in potable water is one of the lowest. Radium-226 and the products of its decay are very dangerous for human health, and adequate assessment of environmental contamination with this isotope is very important [17].

The behavior of radium in soils depends on its chemical properties, physicochemical status, and concentration. The textural and mineralogical soil characteristics; the organic matter content; and the presence of some ions, mobile colloids, complexing agents, and other components in the soil solution are also important. In addition to the chemical properties of the nuclide, its migration capacity is determined by the water and temperature regimes and by the processes related to the living activity of plant roots and microorganisms [15, 16, 18, 22].

OBJECTS AND METHODS

We studied podzols in the area of petroleum production in the Nogliki district of northeastern Sakhalin. Three soil pits were examined. Pit 1 was found in the peripheral part of the petroleum-production area at a distance of 50 m from the slurry pit. The vegetation in this area was thin, and the grass cover was virtually absent. The topsoil horizons were strongly mixed in the course of the reclamation and leveling works on the plot. Pit 2 was dug at a distance of 70 m from pit 1. This area was separated from the industrial plot by a 0.5-m-high ground levee. The plant cover was represented by the overgrowing burnt forest with larch, mountain pine, cowberry, and mosses. Charcoal particles were abundant in the upper soil horizons. Pit 3

Table 1. Chemical properties of podzols on the petroleum-production plot and adjacent area

Horizon	Depth, cm	pH		TAc, mmol(+)/100 g	Exchangeable cations, mmol(+)/100 g			Base saturation	C_{org}	Ash content	OHC
		water	salt		Ca^{2+}	Mg^{2+}	total	%			mg/kg
Pit 1 (petroleum-production plot)											
A + E	0–10	5.16	3.88	8.65	2.27	5.00	7.27	45.7	1.54	–	167.0
B2	0–20	5.36	3.96	4.61	1.18	0.71	1.89	29.2	0.30	–	32.1
B1 + B2	10–30	5.42	3.80	4.61	0.62	1.66	2.28	33.1	0.74	–	25.2
B3	30–42	5.40	3.75	4.61	1.66	0.83	2.49	35.1	0.11	–	0.0
BC	42–60	5.51	3.61	4.82	2.13	0.85	2.98	38.2	0.16	–	7.7
BC	60–80	5.57	3.69	3.19	2.27	1.14	3.41	51.7	0.12	–	21.0
C	80–100	5.64	3.66	3.26	2.52	1.15	3.67	53.0	0.14	–	42.1
Pit 2 (adjacent area)											
O + AT	0–6	4.36	3.39	35.80	8.68	0.92	9.60	21.1	–	54.12	1619.0
AE + E	6–10	4.37	3.14	16.90	10.91	0.68	11.59	40.7	0.67	–	610.0
B1fe	10–16	4.88	4.08	8.45	5.82	0.21	6.03	41.6	1.12	–	55.3
B2	16–31	5.43	4.00	4.82	3.19	0.21	3.40	41.4	0.37	–	51.3
B3	31–54	5.59	3.82	5.98	2.45	1.23	3.68	38.1	0.13	–	84.0
BC	54–69	5.56	3.79	4.92	1.89	0.76	2.65	35.0	0.13	–	30.9
BC	69–83	5.60	3.74	4.42	2.22	0.74	2.96	40.1	0.15	–	54.5
C	83–100	5.64	3.71	4.32	2.69	1.22	3.91	47.5	0.13	–	43.0
Pit 3 (background soil)											
O + AT	0–4	4.61	3.96	28.70	7.34	0.75	8.09	22.0	–	43.10	320.0
AE + E	4–15	4.58	4.00	1.63	1.47	0.31	1.78	52.2	0.87	–	15.3
B1fe	15–20	4.92	4.04	1.60	1.19	0.29	1.48	48.1	0.92	–	0.0
B2	20–36	5.52	3.89	0.76	0.24	0.30	0.54	41.5	0.22	–	0.0
B3	36–64	5.68	3.98	0.95	0.23	0.23	0.46	32.6	0.09	–	76.6
BC	64–100	5.61	3.82	0.36	0.93	0.29	1.22	77.2	0.10	–	70.5
C	100–120	5.62	3.76	0.23	1.10	0.31	1.41	86.0	0.09	–	55.7

TAc is the total acidity.

characterized the background soil at a distance of about 1500 m from pits 1 and 2. The plant cover was similar to that on the second plot. The surface of the soil and the upper soil horizons on plots 2 and 3 did not have the features of mechanical disturbance and petroleum contamination.

Soil samples were taken from the genetic horizons; in the thick horizons, they were taken from each 20-cm-thick layer. In all the samples, the determinations of the pH (in water and KCl extract) were performed using the potentiometric method; the total acidity was determined by the Kappen method in the TsINAO modification; the organic carbon content, by Tyurin's method; the contents of exchangeable Ca^{2+} and Mg^{2+}, by the trilonometric method [1]; and the content of oil hydrocarbons (OHC), by infrared spectrometry [14].

The specific activities of radium-226 and thorium-232 were also determined in all the samples via measuring the radiation of their decay products by gamma spectrometry [10]. It is considered that the products of decay of thorium-232 are in equilibrium in the uncontaminated soils. Thus, the data on the gamma radioactivity of these products characterize the activity of this isotope. Under possible radioactive contamination by natural radionuclides from stratal water rich in radium-226 and radium-228, the specific activities of gamma-emitting isotopes included in the decay chain of thorium-232 might be related to the specific activity of radium-228 [24].

The particular forms of radium-226 were determined in three samples taken from each soil profile, including the upper organic, the middle illuvial, and the deep (parent material) horizons. We used a traditional method of sequential extraction [6]. The specified forms were as follows: water-soluble (distilled water), exchangeable (1 M CH_3COONH_4, pH 4.8), mobile (nonexchangeable, bound with organic matter

Table 2. Activity of radium-226 and radium-228 in podzols of the petroleum-production plot and adjacent areas

Horizon	Depth, cm	Radium-226	Radium-228
		Bq/kg	
Pit 1 (oil-production plot)			
A + E	0–10	19.97 ± 1.31	34.75 ± 1.89
B2	0–20	23.43 ± 1.55	43.48 ± 2.36
B1 + B2	10–30	24.53 ± 1.57	44.40 ± 2.40
B3	30–42	23.43 ± 1.44	37.81 ± 2.03
BC	42–60	21.35 ± 1.36	36.99 ± 1.98
BC	60–80	19.28 ± 1.24	34.02 ± 1.83
C	80–100	22.41 ± 1.44	36.26 ± 1.97
Pit 2 (adjacent area)			
O + AT	0–6	12.62 ± 1.75	26.73 ± 1.89
AE + E	6–10	20.93 ± 1.48	30.37 ± 1.71
B1fe	10–16	20.19 ± 1.40	31.60 ± 1.76
B2	16–31	21.55 ± 1.38	34.89 ± 1.89
B3	31–54	22.42 ± 1.45	42.36 ± 2.26
BC	54–69	24.42 ± 1.54	40.10 ± 2.16
BC	69–83	22.99 ± 1.45	38.12 ± 2.06
C	83–100	23.15 ± 1.48	38.35 ± 2.06
Pit 3 (background soil)			
O + AT	0–4	15.61 ± 6.75	21.52 ± 6.24
AE + E	4–15	27.97 ± 3.05	24.82 ± 2.73
B1fe	15–20	25.11 ± 2.85	29.64 ± 2.87
B2	20–36	25.64 ± 2.98	32.24 ± 3.07
B3	36–64	31.85 ± 3.37	40.28 ± 3.50
BC	64–100	30.90 ± 3.16	36.43 ± 3.19
C	100–120	24.92 ± 2.95	33.67 ± 3.11

and oxides and hydroxides of iron and manganese; 1 M HCl), and acid-soluble (bound with aluminosilicates (sorbed on the surface of the crystal lattices) and bonded with amorphous forms of soil minerals; 6 M HCl). The residual form was determined by the method of fusing with Na_2CO_3.

In the extracts, other natural radionuclides were removed via sorption on $Fe(OH)_3$, and the radium isotopes were coprecipitated with $BaSO_4$ [12]. The specific activity of the radium-226 was measured using an alpha-radiometric method with due account for the alpha activity of the decay products of this isotope [3, 11].

RESULTS AND DISCUSSION

The background soil (pit 3) is a low-humus iron–humus-illuvial shallow loamy sandy podzol developed from marine deposits [9]. This soil is characterized by the very strongly acid and strongly acid reaction in the entire profile. The content of exchangeable bases is low (the degree of unsaturation reaches 78% in the upper horizons) (Table 1). The organic horizons are thin and contain abundant weakly decomposed plant residues attesting to the low decomposition and mineralization rates typical of the soils of Sakhalin [8]. The organic carbon content in the mineral horizons does not exceed 1%, and its distribution has a clearly pronounced eluvial–illuvial pattern.

The content of oil hydrocarbons (OHC) in the organic and mineral horizons does not exceed 320 and 77 mg/kg respectively. It is known that the organic horizons of podzols in the background areas of Sakhalin contain 34–140 mg/kg of oil hydrocarbons [23]. In the organic horizons of uncontaminated soils of petroleum-producing regions, the content of oil hydrocarbons may be as high as 500 mg/kg and more [13, 19]. A higher content of hydrocarbons in the organic horizons in comparison with the mineral horizons can be related to the accumulation of hydrocarbons synthesized by methane-producing bacteria from plant remains [7].

The soil near the industrial plot (pit 2) is represented by a high-humus iron–humus-illuvial shallow loamy sandy podzol developed from marine deposits. It is characterized by the somewhat lower pH values in the entire profile. The content of exchangeable bases is higher than that in the background podzol. The degree of unsaturation with bases remains high (up to 79% in the upper horizons) because of the high total acidity. The organic carbon content in the mineral horizons does not exceed 1.12%, and its distribution has an eluvial–illuvial pattern.

The content of oil hydrocarbons in the organic and upper mineral horizons reaches 1619 and 610 mg/kg, respectively, which is five and eight times higher than in the background soil. Visible evidence of petroleum contamination on the surface and in the profile of this soil are absent, so the increased content of hydrocarbons in comparison with the background soil may be related to the close position of the second soil to the oil well and to the aerial contamination of the territory with light-weight fractions of hydrocarbons.

The soil of the industrial plot (pit 1) is a loamy sandy technopodzol developed from marine deposits [4]. It is mechanically disturbed; the litter horizon is absent, and the upper soil horizons (to the depth of 40 cm) are strongly mixed due to reclamation and surface leveling works on the plot.

The technopodzol has a very strong acid reaction in the entire profile. The content of exchangeable bases is higher in comparison with the background soil and slightly lower in comparison with the soil on the adjacent plot. The same is true for the total acidity. The degree of unsaturation is 71% in the upper horizons. The humus content is relatively low; the maximum is found in the upper layer representing a mixture of the A and E horizons of the natural soil. In the deep mineral horizons, the humus content does not exceed 0.74%. The highest content of hydrocarbons

Table 3. Forms of radium-226 in podzols of the petroleum-production plot and adjacent areas, % of the total content

Horizon	Depth, cm	Water-soluble	Exchangeable	Mobile	Acid-soluble	Residual
Pit 1 (oil-production plot)						
A + E	0–10	0.8 ± 0.2	14.6 ± 1.2	8.9 ± 1.3	5.2 ± 1.0	70.6 ± 7.7
B3	30–42	0.5 ± 0.2	20.6 ± 1.4	10.1 ± 0.8	7.7 ± 0.8	61.1 ± 6.6
C	80–100	1.1 ± 0.2	37.0 ± 3.0	9.5 ± 1.5	4.9 ± 1.4	47.5 ± 7.6
Pit 2 (adjacent area)						
O + AT	0–6	0.9 ± 0.3	4.1 ± 0.8	9.4 ± 1.1	7.8 ± 1.0	77.8 ± 11.7
B3	31–54	0.8 ± 0.2	24.5 ± 1.6	12.3 ± 0.8	10.9 ± 0.8	51.6 ± 5.3
C	83–100	0.9 ± 0.3	36.4 ± 3.6	7.0 ± 1.0	1.7 ± 0.2	53.9 ± 10.4
Pit 3 (background soil)						
O + AT	0–4	1.6 ± 0.3	3.9 ± 0.6	14.8 ± 1.5	15.5 ± 1.6	64.2 ± 9.6
B3	36–64	0.7 ± 0.2	22.0 ± 1.5	8.9 ± 0.8	5.0 ± 0.5	63.4 ± 6.9
C	100–120	0.9 ± 0.3	27.0 ± 2.5	5.8 ± 0.7	6.2 ± 0.7	60.1 ± 9.5

(167 mg/kg) is in the upper layer. In the deeper horizons, the content of hydrocarbons does not exceed 42 mg/kg.

Note that the soils of the industrial plot and the adjacent area differ from the background soil in the higher total acidity and higher content of exchangeable cations; they have lower pH KCl values, which may be related to the properties and composition of the stratal waters contaminating these plots [21].

The specific activities of radium-226 and radium-228 are relatively low (Table 2). In the background soil (pit 3), the minimum activity is in the organic horizons. This can be explained by the relatively high content of exchangeable calcium, which competes with radium for sorption sites; the adsorption of calcium on the surface of mineral particles prevents the adsorption of radium [16]. In the mineral horizons, the activities of radium isotopes are higher and reach their maximum in the lower part of the illuvial layer.

In the mechanically undisturbed soil of the second plot (pit 2), the specific activity of radium-226 is somewhat lower than in the background soil, and its distribution pattern in the soil profile is the same (with a maximum in the lower horizons). At the same time, the specific activity of radium-228 is higher than that in the background soil. In the soil of the industrial plot (pit 1), the lowering of the specific activities of the radium isotopes in the upper soil horizons and the accumulation of exchangeable calcium are not very pronounced in comparison with the second plot.

Thus, the soils of the petroleum-production plot and the adjacent area do not show the accumulation of radium isotopes in comparison with the background soil. At the same time, the distribution patterns of the particular forms of radium-226 in the background soil and in the soils of the impact zone are different (Table 3).

In the background soil (pit 3), the portion of water-soluble radium-226 is not high in the entire profile. The portion of exchangeable forms is the smallest in the organic horizon (3.9%) and increases in the mineral horizons due to the lower competition between radium-226 and calcium for exchangeable positions. The portion of radium-226 bound with organic matter and oxides and hydroxides of iron and manganese decreases down the soil profile in conjunction to the organic carbon content. A similar distribution is typical of the acid-soluble (bound with aluminosilicates and amorphous soil minerals) form of radium-226. The largest portion of radium-226 (60.1–64.2%) is found in the crystal lattices of primary minerals. The changes in this characteristic along the soil profile are insignificant.

In the soils contaminated with stratal waters (pits 1 and 2), the distribution patterns of radium-226 are different. The portion of the exchangeable form sharply increases in the parent material, and the portion of the mobile and acid-soluble form increases in the illuvial horizons and decreases in the upper organic horizons.

It is known that the sorption of technogenic radionuclides depends on the initial form of these elements and on the nature of the adsorbing substances. Radium transported to the surface of the soil with chloride–calcium stratal waters is firmly fixed by the organomineral sorption complex of the humus horizons. The mobility and biological availability of radium in the contaminated soils may be even lower than that in the uncontaminated soils because of its isomorphic entering into the crystal lattices along structural defects, precipitation and coprecipitation, and complex formation with low-mobile fractions of the organic matter [16, 20, 22].

The high portion of the exchangeable form of radium-226 in the deep horizons of the podzols of contaminated plots (1 and 2) in comparison with the background podzol (plot 3) points to the fact that the soils were contaminated with stratal waters not only from the surface but also with subsurface water flows from the slurry pit.

CONCLUSIONS

The significant accumulation of radium-226 is observed in the podzols of northeastern Sakhalin contaminated with slightly saline and slightly radioactive stratal water. However, the distribution patterns of the particular forms of this radionuclide in the contaminated soils are different from those in the background soils. The highest portion of radium-226 is in firmly fixed forms is inherited from the parent material. Water-soluble radionuclides entering the soil are accumulated in the exchangeable and mobile forms in the deep horizons of the contaminated soils. This attests to the contamination of the soils with stratal waters not only from the surface but also with the subsurface water flows from the adjacent slurry pit.

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