Comparison of Pavlotskaya and Tessier Methods for Assessment of Radionuclide Speciation in Soils

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Studied soil specimen

Soil specimen collected in 2001 in the **podzolic horizon** of a sod–low-podzolic sandy soil formed under a broad-leaved–coniferous forest (Krasnogorsk district, Bryansk oblast, Russia).

The activities of natural radionuclides are consistent with the levels typical for soils of European Russia.

Studied soil specimen

Parameter	Value
pH H_2O	5.0
pH KCl	3.8
C_{org} content	0.25%
Total acidity	5.25 cmol (+)/kg
Exchangeable Ca^{2+} content	1.37 cmol (+)/kg
Exchangeable Mg^{2+} content	0.74 cmol (+)/kg
V (bases saturation degree)	29%
Granulometric composition, %	
0.25–1 mm	49.4
0.05–0.25 mm	45.8
0.01–0.05 mm	1.7
0.005–0.01 mm	0.9
0.001–0.005 mm	1.7
<0.001 mm	0.5

Studied soil specimen

Parameter	Value
Gross content of chemical elements, mg/kg	
Fe	2120
Mn	264
Sr	36
Pb	26
Ni	7
Co	0.30
Specific activities of radionuclides, Bq/kg	
^{226}Ra	43.3
^{232}Th	10.2
^{238}U	28.9

Sequential extraction procedure

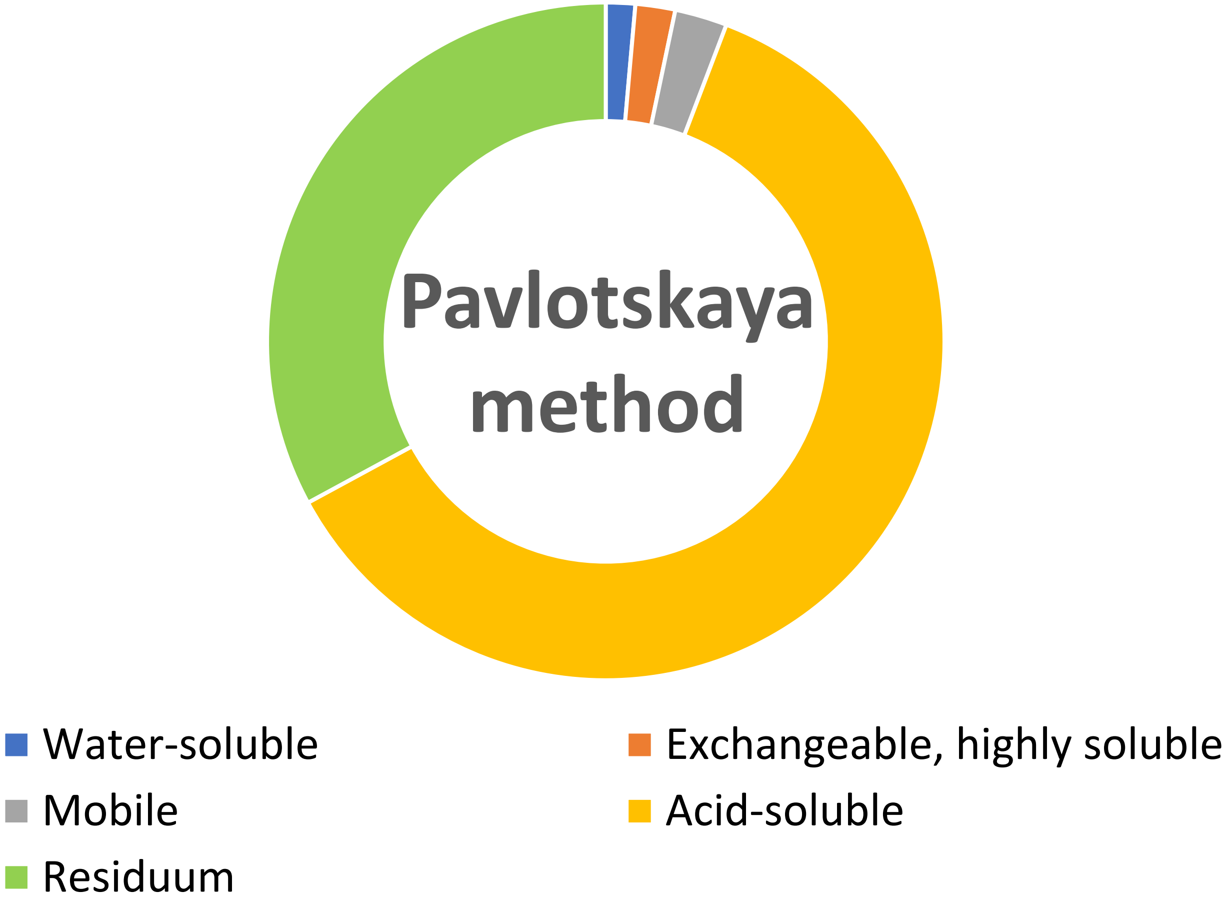
Pavlotskaya method		
Form	Reagent	Experimental conditions
First quantity		
Water-soluble	H_2O	solid-to-liquid ratio = 1:5, t = 5 min, 20°C
Exchangeable, highly soluble	1 mol/dm^3 CH_3COONH_4, pH 4.8	solid-to-liquid ratio = 1:10, t = 1 h, 20°C
Mobile	1 mol/dm^3 HCl	solid-to-liquid ratio = 1:10, t = 1 h, 20°C
Acid-soluble	6 mol/dm^3 HCl	solid-to-liquid ratio = 1:10, t = 1 h, 20°C
Residuum	Sintering with Na_2CO_3	850°C
Second quantity		
In amorphous compounds	0.2 mol/dm^3 $(NH_4)_2C_2O_4$ in 0.1 mol/dm^3 $H_2C_2O_4$	solid-to-liquid ratio = 1:20, t = 1 h, 20°C, twofold treatment
Residuum	Sintering with Na_2CO_3	850°C

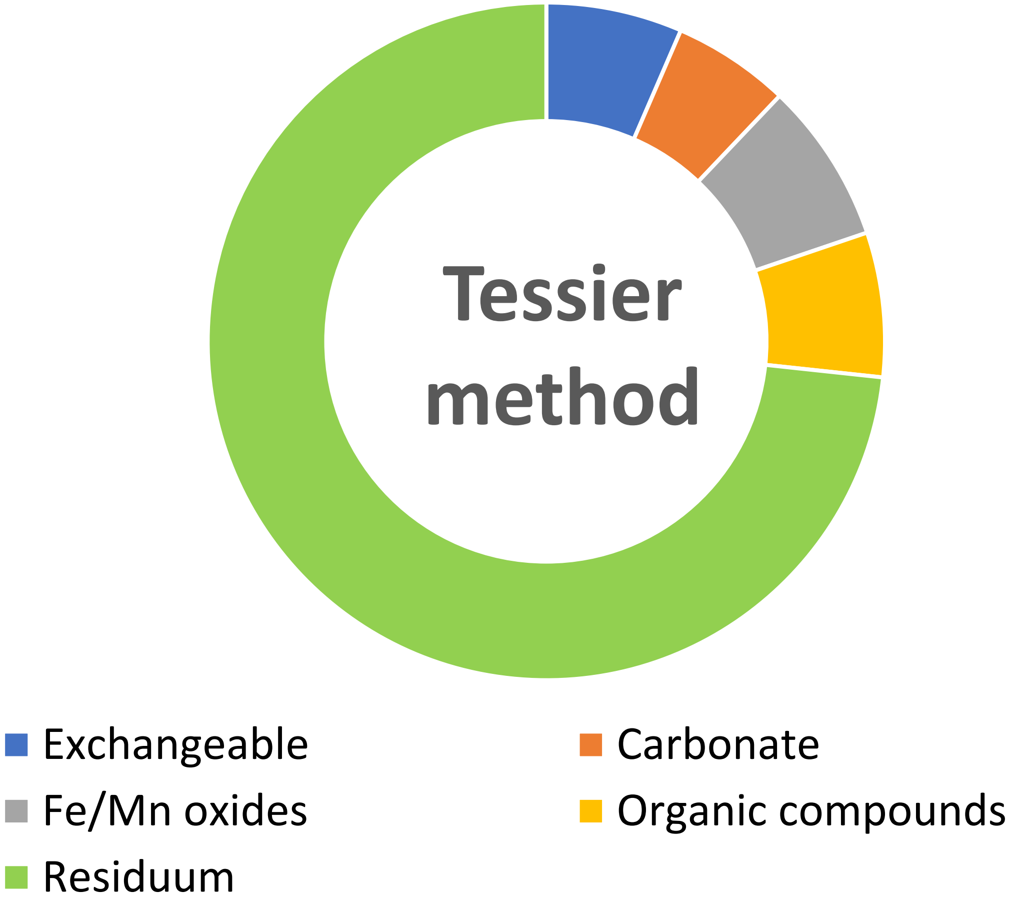
Goryachenkova, T.A., Kazinskaya, I.E., Novikov, A.P., et al., Comparison of methods for assessing plutonium speciation in environmental objects, *Radiochemistry*, 2005, vol. 47, no. 6, pp. 599–604.

Tessier method		
Form	Reagent	Experimental conditions
Exchangeable	1 mol/dm^3 $MgCl_2$, pH 7	solid-to-liquid ratio = 1:8, t = 1 h, 20°C
Carbonate (specifically sorbed)	1 mol/dm^3 CH_3COONa, pH 5	solid-to-liquid ratio = 1:8, t = 1 h, 20°C
Fe/Mn oxides	0.4 mol/dm^3 $NH_2OH \cdot HCl$ in 25% CH_3COOH, pH 1	solid-to-liquid ratio = 1:20, t = 1 h, 20°C
Organic compounds	30% H_2O_2 (5 parts) mixed with 0.02 mol/dm^3 HNO_3 (3 parts)	solid-to-liquid ratio = 1:8, t = 2 h, 85°C
	30% H_2O_2, pH 2	solid-to-liquid ratio = 1:3, t = 3 h, 85°C
	0.8 mol/dm^3 CH_3COONH_4 in 5% HNO_3	solid-to-liquid ratio = 1:20, t = 30 min, 20°C
Residuum	Sintering with Na_2CO_3	850°C

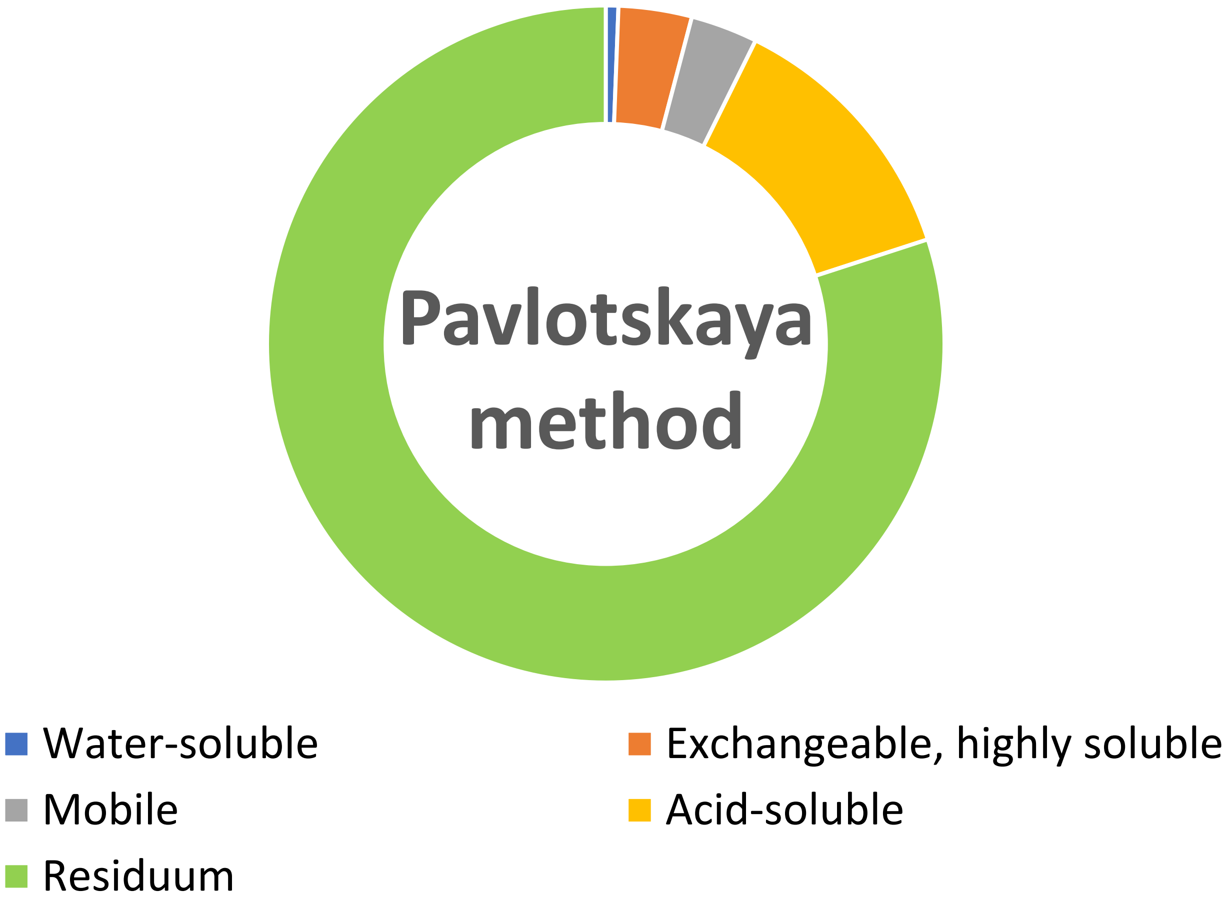
Tessier, A., Campbell, P.G.C., and Bisson, M., Sequential extraction procedure for the speciation of particulate trace metals, *Anal. Chem.*, 1979, vol. 51, no. 7, pp. 844–851.

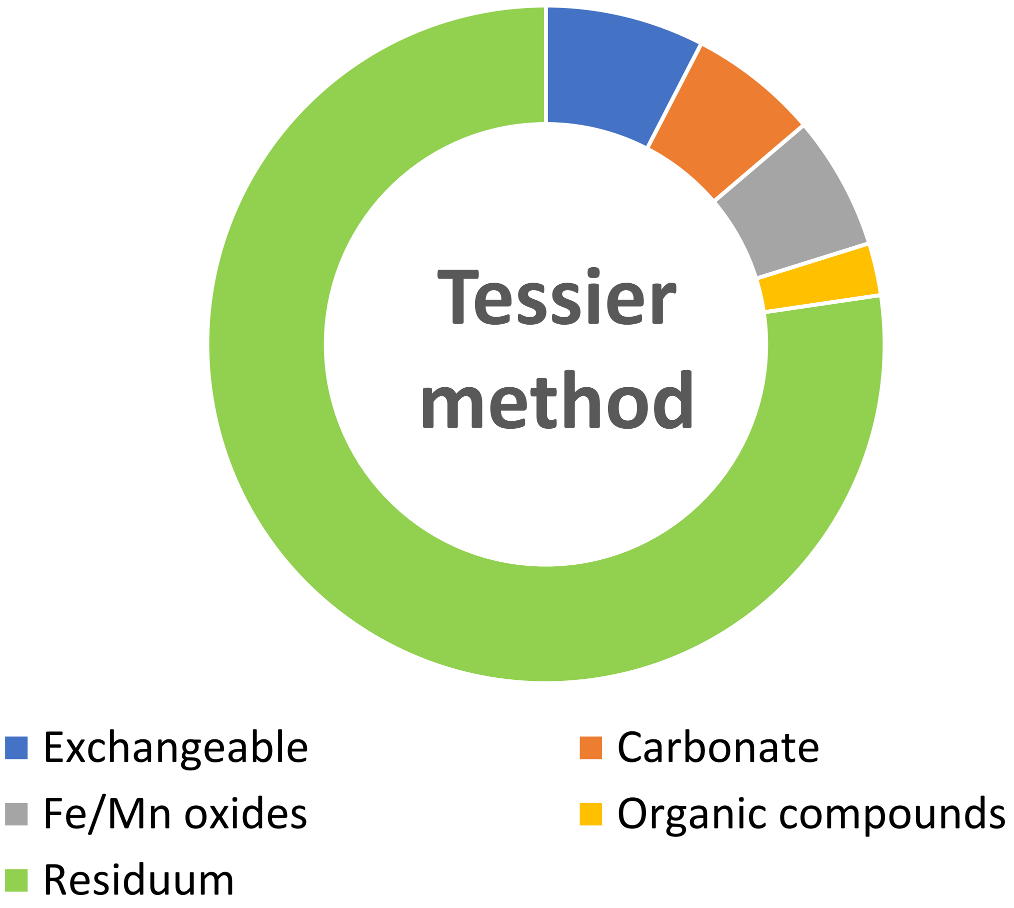
Radium-226


Pavlotskaya method
Water-soluble
Exchangeable, highly soluble
Mobile
Acid-soluble
Residuum

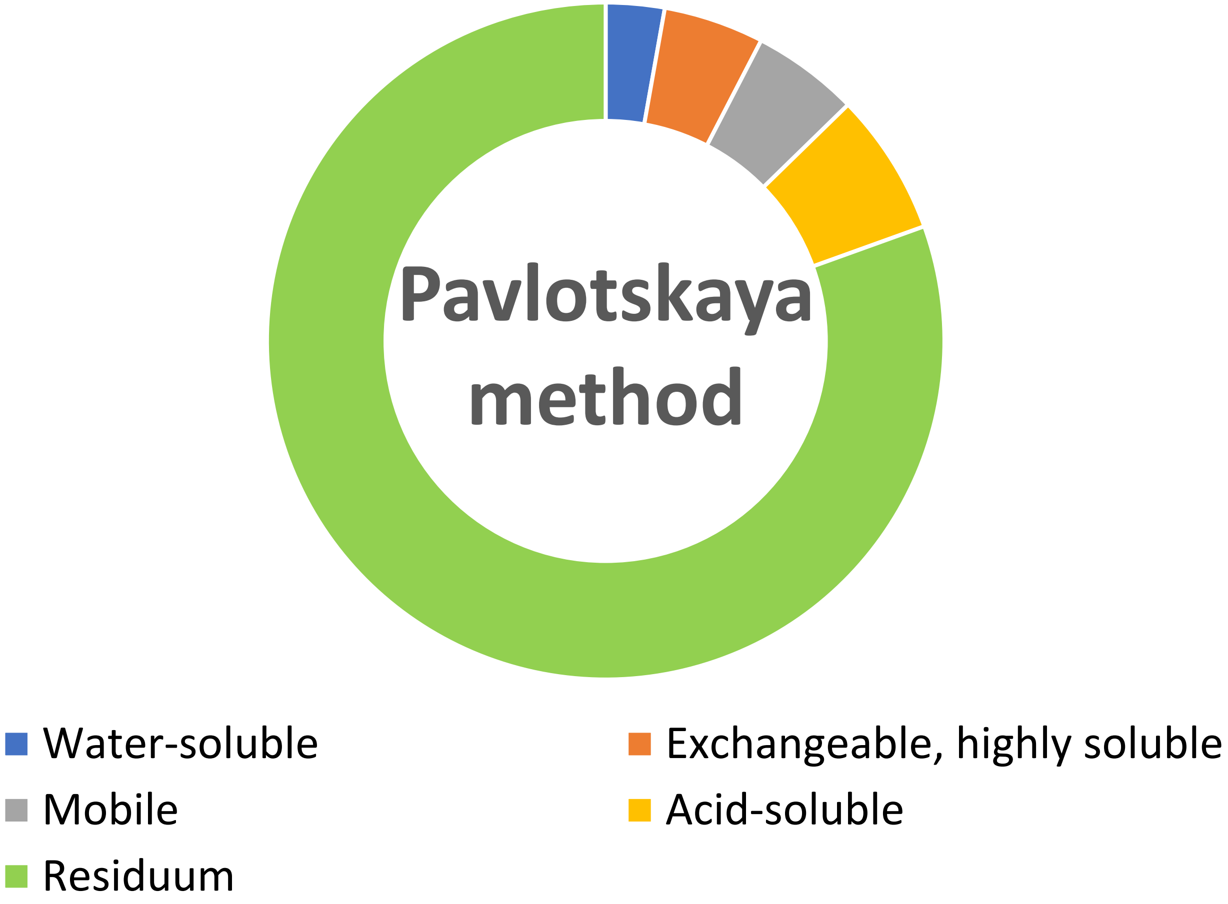

Tessier method
Exchangeable
Carbonate
Fe/Mn oxides
Organic compounds
Residuum

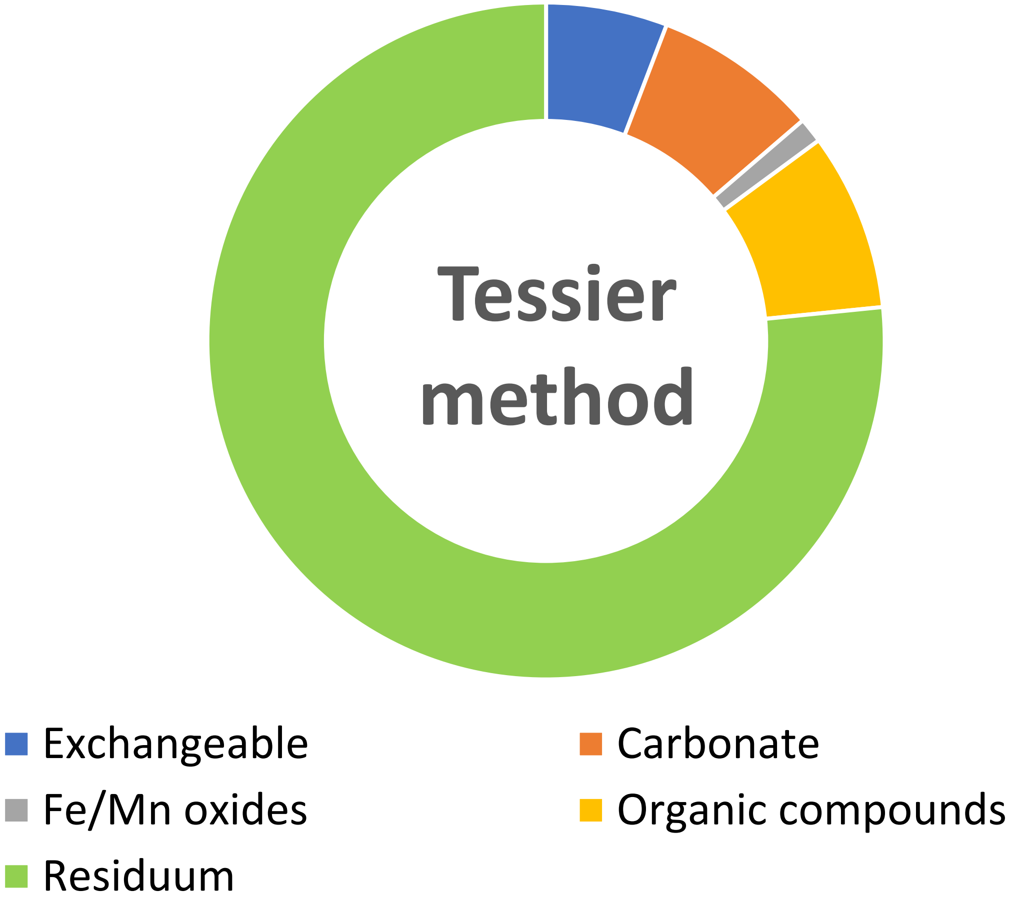
Uranium-238


Pavlotskaya method
Water-soluble
Exchangeable, highly soluble
Mobile
Acid-soluble
Residuum


Tessier method
Exchangeable
Carbonate
Fe/Mn oxides
Organic compounds
Residuum

Thorium-232


Pavlotskaya method
Water-soluble
Exchangeable, highly soluble
Mobile
Acid-soluble
Residuum


Tessier method
Exchangeable
Carbonate
Fe/Mn oxides
Organic compounds
Residuum

Conclusions

- The application of the above methods for the speciation assessment of natural radionuclides (^{226}Ra, ^{232}Th, and ^{238}U) gives poorly consistent results. The Tessier method indicates higher contents of compounds available to plants and mobile compounds in comparison with the Pavlotskaya method. The main reason behind this may be the complexity of the soil chemistry of ^{232}Th and ^{238}U that feature strong tendency for hydrolysis and complex formation; in addition, their behavior may be affected by various carriers. Therefore, these elements form a broad range of compounds that change one into another with changes in the chemical conditions; this complicates accurate comparison of the composition of their forms extracted by the reagents.

Conclusions

- An advantage of the Tessier method is the selective extraction of radionuclides bonded with organic matter, while in the Pavlotskaya method, radionuclides bonded with organic matter constitute parts of the mobile and acid-soluble fractions. On the other hand, the Tessier method does not include the extraction of water-soluble compounds constituting the most available and mobile portion of the soil radionuclide pool. In addition, the Tessier method does not include the extraction of compounds bonded with crystalline iron and aluminum oxides, which makes comprehensive assessment of the behavior of natural radionuclides (^{226}Ra, ^{232}Th, and ^{238}U) impossible.