

Application of Rotating Coiled Columns to the Fractionation of Soil Particles and to the Sequential Extraction of Heavy-Metal Species from Silty, Dusty, and Sandy Fractions

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Abstract—A complex procedure has been developed for evaluating the degree of soil contamination. Rotating coiled columns (RCCs) were used for both the fractionation of soil samples by their grain-size composition and the sequential extraction of heavy-metal species from silty, dusty, and sandy fractions. During the extraction of heavy-metal species, the soil fraction to be analyzed was retained in the column as a stationary phase, while aqueous solutions of extracting agents (mineral salts, acids, and complexing compounds) were sequentially pumped through the heterogeneous sample. The sequential extraction of element species from various soil fractions was carried out in the dynamic mode favorable to more complete extraction of metals. The use of RCCs allows the extraction of various heavy-metal species from soils to be performed in accordance with their grain-size composition. The process of the extraction of metal species can be automated, and in this case the losses of sample components are reduced to a minimum.

At present, environmental monitoring has become one of the main problems of modern ecology. The necessity of environmental control is generated by the ever-growing anthropogenic factor, which affects nature. The problem of soil contamination occupies a special place in the system of monitoring, because soils are the main link of the ecosystem. Among the numerous groups of contaminants, heavy metals (Hg, Pb, Cd, Zn, etc., and As) belong to one of the most dangerous, because their technogenic accumulation in the environment grows rapidly. Not only can these microelements inactivate physiologically active compounds and disturb metabolism, growth, and development processes, but they can also break the integrity of the entire ecosystem [1–3]. To estimate the detrimental role of heavy metals in various natural media, it is important to determine not only the total concentration but also their speciation in environmental objects, because microelements not only can occur as ions and dissolved low-molecular compounds but can also be bound with natural macromolecules and solid particles.

The grain-size composition of a soil has a great impact on the distribution of heavy metals in the soil. Fine fractions (silty and dusty) containing clay minerals and organic compounds with a high absorptive capacity concentrate the main part of heavy metals, as distinct from a sandy fraction [1]. This is explained by the fact that heavy metals differ in their affinity to certain substrates. Thus, heavy-metal ions with a small ionic radius, for example, Cr^{3+} , Zn^{2+} , Ni^{2+} , Cu^{2+} , and

Co^{2+} , not only can occur in the exchange form but also can isomorphously occupy octahedral positions in clay minerals. The Pb^{2+} and Cd^{2+} ions cannot be fixed in the octahedron because of their large radius. They not only can be actively bound by humic substances in the exchange form, but also can form stable organic mineral complexes, reducing the lability of metals [2, 3]. Iron oxides should also be assigned to the main “carriers” of heavy metals in soils. It should be noted that not only complexes of clay minerals with an organic substance but also iron and aluminum hydroxides take an important part in the accumulation of heavy metals. It was shown that these complexes absorb microelements from three to four times more intensely than pure clay minerals, because of the presence of organomineral films on their surface. The heavy fraction with the density $\rho = 2.75$ of the coarse-grained part of soil-forming rocks and soils is also saturated with heavy metals [2, 3]. However, the fraction of heavy metals (hornblende, ilmenite, zircon, and epidote) in the substrate is small and cannot significantly affect the balance of metals. It follows from the above that, for the diagnostics of the soil state in local monitoring, it is primarily necessary to determine the speciation of metals in fine (silty and dusty) fractions.

At present, sedimentation and sequential extraction carried out in the batch mode are used, respectively, in each of the obtained fractions for the separation of soil samples by their grain-size composition and for the extraction of various element species. The sedimenta-

tion technique is based on the difference in the sedimentation rates of solid particles in an aqueous medium under the action of gravitation. The process is sufficiently routine and prolonged. For example, several days were required for the extraction of the silty soil fraction [4].

Various procedures of sequential extraction in the batch mode are used for the extraction of element species [5–9].

Depending on the chemical nature of extracting agents, heavy metals occurring in various forms and compounds are extracted from soils. Three forms are most available: the exchange form, the carbonate form, and elements bound with manganese oxides. In the exchange form, the metal is bound with the matrix by weak electrostatic forces. The coprecipitation process favors the fixation of microelements on the substrate in the carbonate form. In this case, the liberation of a microelement can be achieved upon a change in the ionic strength of the medium responsible for the adsorption–desorption processes or upon a decrease in pH. A change in the redox potential serves as the condition for the extraction of heavy metals bound with magnesium oxides.

Various element species are extracted by one-step batch extraction procedures accepted in Russia using 1 M HNO_3 (extraction of acid-soluble forms), a 1 M solution of $\text{CH}_3\text{COONH}_4$ (exchange forms), or an acetate–ammonia buffer solution with pH 4.8 (mobile forms).

More comprehensive data on the speciation of elements can be obtained using various sequential extraction procedures [5–9]. The sequential extraction procedure developed by McLaren and Crawford for the extraction of various Cu, Zn, and Pb species [6] can be mentioned as an example. According to this procedure, the following forms are extracted: the exchange and acid-soluble forms (extracted with a 0.05 M solution of CaCl_2), the carbonate form (2.5% CH_3COOH), elements bound with organic substances (0.1 M $\text{K}_4\text{P}_2\text{O}_7$ + 0.1 M KOH), elements bound with Mn, Fe, and Al oxides (0.1 M $\text{H}_2\text{C}_2\text{O}_4$ + 0.175 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$, pH 3.25), and the residual form (HF).

It should be noted that a drawback of all the sequential extraction procedures in the batch mode is their laboriousness and duration. Moreover, it is known that the processes proceeding in nature are always dynamic, while all the proposed procedures are based on a sequence of one-step extractions. Hence, it is reasonable to perform extraction in the dynamic mode for a more correct evaluation of the state of elements in natural conditions.

In our work, the separation of solid particles and the extraction of various heavy-metal species were performed in rotating coiled columns (RCCs). An RCC represents a Teflon tube spooled on a cylindrical drum, which rotates about its axis and simultaneously about

the central axis of a planet centrifuge. As a result of planetary motion, a complex asymmetrical field arises, which acts on the particles occurring in the column. This is responsible for various migration velocities of mixture components along the column walls in the mobile phase flow. Since 1970, RCCs have been successfully used in liquid chromatography with a free stationary phase (LCFSP). The principal possibility of using a planet centrifuge for not only the separation of dissolved substances but also the fractionation of particles of model and natural samples was first demonstrated in the laboratory of concentration at the Vernadsky Institute of Geochemistry and Analytical Chemistry. The regularities of the behavior of particles in a column were studied using the separation of model spherical particles (latexes and silica gels) and natural nonspherical particles of quartz sand as an example [10, 11]. The advantage of using RCCs for the determination of the speciation of metals as compared to the conventional sequential extraction procedure was also demonstrated [7, 12]. The extraction of various metal species was performed by the Kerstner–Forstner procedure (a version of the Tessier procedure), according to which the following microelement species were extracted: the exchange form, the “carbonate” form, elements bound with manganese oxides, elements bound with iron and aluminum oxides, and the sulfide–organic form [8]. The first three forms are most available and, hence, most dangerous for living organisms, because the bond between the matrix and the microelement in this case is characterized by lability.

It is worth noting that the processes of the fractionation of particles and the sequential extraction of microelement species are carried out in the dynamic mode, which is favorable to more complete extraction of elements. In this case, the losses of the sample are reduced to a minimum and the process of the extraction of metal species can be automated.

The goal of this study was to demonstrate the advantages of using RCCs for the development of a complex method of soil monitoring and to obtain more comprehensive data on the distribution of heavy-metal species in various fractions (in grain-size composition: silty, dusty, and sandy) of the sample to be analyzed.

EXPERIMENTAL

Analyzed samples. Two samples of contaminated soil were studied: a standard sample (SRM 2710 NIST) and a real sample taken from the Moscow region. The real sample of soil was sifted through a sieve with a pore diameter of 250 μm . The total concentration of metals in the samples is indicated in Table 1. The total concentration of metals in the real sample was determined by the ICP MS technique after the decomposition of the sample. The reagents used as the mobile phases for the extraction of various species of metals in the initial sample and in soil fractions are listed in Table 2.

Table 1. Total content of some heavy metals in the standard (SRM-2710) and real (taken from the Moscow region) soil samples ($\mu\text{g}/\text{kg}$)

Soil sample	Zn	Pb	Cd	Cu
Standard sample (SRM-2710)	6952 \pm 91	5532 \pm 80	21.8 \pm 0.2	2950 \pm 130
Real sample	406 \pm 8	30 \pm 1	15.0 \pm 0.7	128 \pm 0.5

Apparatus. The separation of the soil sample by its grain-size composition and the extraction of heavy-metal species were carried out on a setup including a model of the planet centrifuge and a peristaltic pump. The centrifuge was equipped with a single-layer column whose revolution radius was $R = 80$ mm and rotation radius was $r = 40$ mm. The column was a fluoroplastic tube (F-4-MB) with an inner diameter of 1.5 mm wound on a cylindrical drum. The column volume (V_c) was 17 mL, and the volume of feeding lines (V_f) was 2 mL. The speed of rotation of the centrifuge column unit equaled its speed of revolution ω and was 150 rpm for the fractionation of the standard sample by its grain-size composition and 80–100 rpm for the real sample. For the sequential extraction of heavy-metal species, $\omega = 600$ –650 rpm.

Procedure. *Fractionation of soil particles by the grain-size composition.* Before the beginning of the experiment, the column was filled with distilled water. The sample to be analyzed (0.5 g soil in 10 mL distilled water) was injected through the peristaltic pump; next, the column was brought into rotation, and the mobile phase (water) was fed to its inlet. The separation of soil into fractions was carried out using a stepwise change of the carrier-liquid flow rate from 1 to 15 mL/min at a constant speed of rotation of the centrifuge, 150 rpm for the standard sample and 80–100 rpm for the real soil sample. The separated fractions were filtered off, dried, and weighed.

Extraction of heavy-metal species from silty, dusty, and sandy fractions. The sequential extraction of heavy-metal species was performed by the Kerstner–Forstner procedure. The soil fraction to be analyzed

was injected into the column as a suspension in 10 mL of 1 M ammonium acetate. The column was brought into rotation, and solutions of extracting agents were fed sequentially at a constant speed of rotation of the centrifuge $\omega = 650$ rpm and the carrier-liquid flow rate $F = 1$ mL/min (hydrogen peroxide was an exclusion). Hydrogen peroxide was injected at the flow rate $F = 0.5$ mL/min to increase the time of reagent contact with the sample, which was favorable to more complete liberation of the metal from the sulfide–organic form. The volume of the separated fractions V was 30–75 mL. These fractions were collected, and the concentration of microelements in each fraction was determined by the ICP MS technique.

Determination methods. *Mass-spectrum analysis.* The concentrations of Cu, Zn, Cd, and Pb in solutions were determined by the ICP MS technique using an X-7 ICP-MS instrument (Thermo Elemental, US).

The concentrations of elements in aqueous solutions were determined quantitatively using samples of reference solutions containing from 1 to 500 $\mu\text{g}/\text{L}$ test elements. To increase the accuracy, barium and strontium were used as internal references. The concentration of these elements in the samples was determined preliminarily by atomic emission spectrometry.

The treatment of mass spectra and the calculations of the concentration of elements in the samples were performed using the mass-spectrometer software. The concentrations of Cu, Zn, Cd, and Pb in the sample were calculated as an average value measured by their isotopes.

The detection limit (DL) was calculated by the equation

$$\text{DL} = c_i + 3s,$$

where c_i is the average value of the concentration of element i in the measurements of twice-distilled water and s is the standard deviation for element i in the measurements of twice-distilled water.

The relative standard deviation for all elements did not exceed 0.3 for the determination of up to 5 DLs of these elements and did not exceed 0.15 for the determination of concentrations > 5 DLs.

Table 2. Kerstner–Forstner sequential extraction scheme

Stage	Reagent	Fraction	Extracted component	Lability	Availability for plants
1	1 M $\text{CH}_3\text{COONH}_4$, pH 7	Exchange, water-soluble	Exchange ions	Labile	Readily available
2	1 M CH_3COOH , pH 5	Acid-soluble	Carbonates	Highly labile	
3	0.01 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ + 0.01 M HNO_3 , pH 2	Readily reducible	Mn oxides	Moderately labile	Moderately available
4	0.1 M oxalate buffer solution, pH 3	Hardly reducible	Amorphous Fe oxides	Weakly labile	Hardly available
5	30% H_2O_2 , pH 2; 1 M $\text{CH}_3\text{COONH}_4$ in 6% HNO_3	Oxidizable	Organic substances and sulfides		
6	Hot HNO_3	Residual	Mineral matrix		Unavailable

Table 3. Results of determination of various heavy-metal species ($\mu\text{g}/\text{kg}$) in the initial standard (SRM-2710) soil sample ($n = 3$; $P = 0.95$)

Me	Exchange	Carbonate	Fraction of elements bound with Mn oxides	Fraction of elements bound with Fe and Al oxides	Organic-sulfide
Zn	1043 \pm 14	626 \pm 7	834 \pm 12	1391 \pm 195	695 \pm 7
Pb	1992 \pm 40	498 \pm 7	1438 \pm 20	1217 \pm 16	331 \pm 4
Cd	15 \pm 1	1.7 \pm 0.1	2.6 \pm 0.1	0.40 \pm 0.01	0.40 \pm 0.01
Cu	1062 \pm 16	265.5 \pm 4.5	678 \pm 14	324.5 \pm 5.1	265.5 \pm 3.4

RESULTS AND DISCUSSION

Fractionation of soil particles. As was mentioned above, a number of regularities in the behavior of solid particles in RCCs was studied previously using latex and silica-gel particles of nonspherical shape as an example [7, 12]. It was shown that the fractionation of a solid sample depends on the design and working parameters of the centrifuge: the type of the kinematic scheme of the planetary gear, the inner diameter of the capillary, the speed of rotation of the centrifuge, the directions of rotation and pumping of the mobile phase, and the inner surface of the column capillary. The separation of particles is also affected by the initial flow rate of the mobile phase and the injected sample volume. In this work, based on the revealed regularities, we selected conditions for the fractionation of the standard soil sample into silty, dusty, and sandy fractions. The grain-size classification by N.A. Kachinckii was taken as the basis, according to which the silty part includes particles from 0.1 to 0.2 μm in diameter; the dusty part, from 2 to 50 μm ; and the sandy part, more than 50 μm .

A planet centrifuge with the type J kinematic scheme of a planetary gear (the directions of rotation and revolution of the device coincide) was used for the separation of the standard soil sample SRM 2710. The content of particles in the sample volume (10 mL) injected into the column was 0.5 g. Three fractions were separated during the experiment. At the speed of rotation of the planet centrifuge $\omega = 150$ rpm and the flow rate $F = 1\text{--}3.5$ mL/min, the particles of the silty fraction are washed off. The total volume of this fraction was 200 mL. At the flow rate $F = 5\text{--}10$ mL/min, the dusty fraction was separated with the total volume equal to 130 mL. The particles of the sandy fraction were displaced from the stopped column with air bubbles at the maximum flow rate $F = 15$ mL/min. This fraction was not further analyzed, because its starting concentration in the entire bulk of the soil sample was not sufficient for the subsequent investigation. The remaining two fractions were filtered off, dried, and weighed. The mass of particles of the silty fraction was 0.3 g and that of the dusty fraction was 0.2 g.

During the fractionation of the real soil sample (42 g), the speed of rotation of the planet centrifuge was 80–100 rpm. At the flow rate $F = 0.7$ mL/min, a silty

fraction was separated with a volume of 75 mL. The dusty fraction 50 mL in volume is washed out at the flow rate $F = 2$ mL/min. At the flow rate $F = 7$ mL/min, a sandy fraction was obtained with a volume of 28 mL. A decrease in column ω down to 80–100 rpm for the separation of the real soil sample allowed the coarse sand fraction to be separated directly in the course of experiment without stopping the column. These fractions were also filtered off, dried, and weighed. The mass of particles of the silty fraction was 0.01 g; that of the dusty fraction, 0.21 g; and that of the sandy fraction, 0.2 g.

Extraction of microelement species from the initial soil sample. As was mentioned above, it is important to determine the speciation of microelements in environmental objects for the estimation of their lability and toxicity. Various sequential extraction procedures are used for the extraction of various heavy-metal species [5, 9].

In our study, special attention was paid to the Kerstner–Forstner scheme, because it allows the concentration of labile forms of metals in soils to be evaluated with sufficient reliability.

Extraction of heavy-metal species from the standard reference sample of soil SRM-2710. At the first stage, the content of heavy-metal species in the initial soil sample was determined (0.5 g). As is demonstrated by Fig. 1 and Table 3, the main part of heavy metals is concentrated in three forms: the exchange form, the form bound with manganese oxides, and the form bound with iron and aluminum oxides. The predominance of the exchange form is observed for all the elements; Cadmium should be mentioned specially, because its content in the exchange form exceeds 60%. It is worth noting that the majority of heavy metals are bound with manganese, iron, and aluminum oxides. Evidently, this fact can be explained by the presence of organomineral films on their surface. Only a small fraction of all the metals is concentrated in the carbonate and sulfide-organic forms. Correspondingly, the most available part of heavy metals in this sample will be fixed in the exchange form and will be bound with manganese oxides.

Extraction of heavy-metal species from the sample of soil taken from the Moscow region. In the case of the sequential extraction of element species from the real

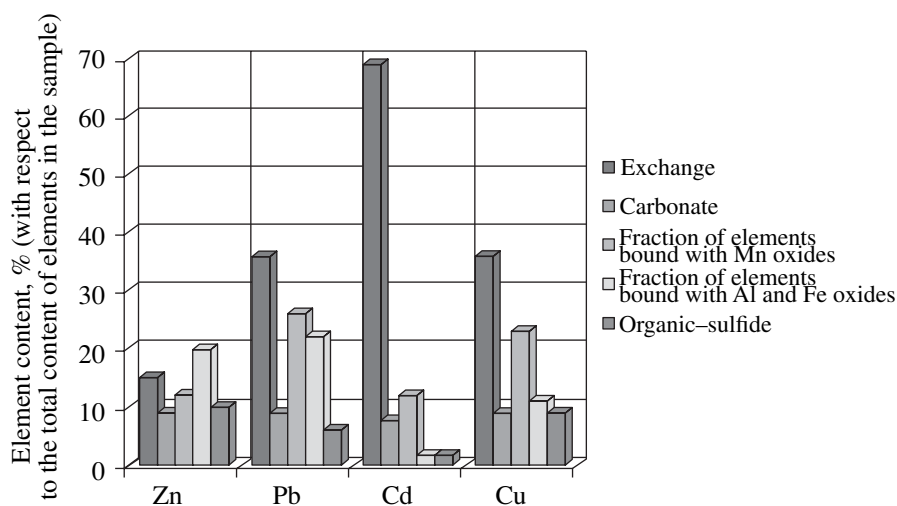


Fig. 1. Use of rotating coiled columns for the fractionation of soil particles and the sequential extraction of heavy-metal species from silty, dusty, and sandy fractions (SRM-2710).

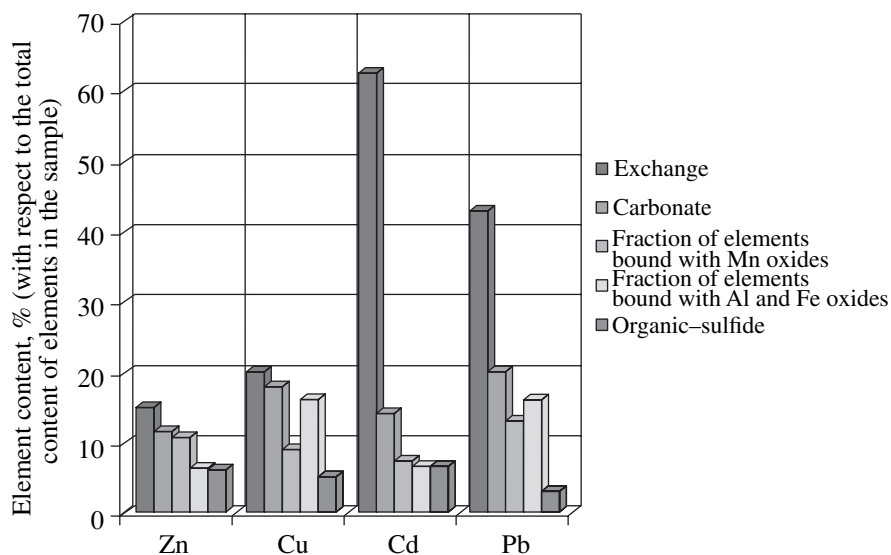


Fig. 2. Use of rotating coiled columns for the fractionation of soil particles and the sequential extraction of heavy-metal species from silty, dusty, and sandy fractions.

sample of soil, the main part of heavy metals is not only distributed among the exchange form and the form bound with manganese, iron, and aluminum oxides but also concentrated in the carbonate form (Fig. 2 and Table 4). As in the case of the standard sample, the predominance of the exchange form (62% Cd) and a considerable contribution of magnesium and iron oxides in the concentration of heavy metals (especially, Cu and Pb) are observed. Correspondingly, the real soil can be dangerous because of the three most available heavy-metal species.

Extraction of microelement species in silty, dusty, and sandy fractions of soil. At the second stage of this

study, the distribution of heavy metals among their labile forms was studied in grain-size fractions of soil.

In the case of the real sample, sequential extraction was applied to the silty (0.01 g), dusty (0.21 g), and sandy (0.20 g) fractions of soil. As is demonstrated by Fig. 3 and Table 5, the silty and dusty fractions of soil contain tens of times more heavy metals than the dusty fraction, which equals them in mass. As was indicated above, the silty and dusty fractions concentrate the main part of elements, because these contain clay minerals and humic substances, which are characterized by a high absorptive capacity. For the sequential extraction of each of the grain-size fractions, a similar pattern is

Table 4. Results of determination of various heavy-metal species ($\mu\text{g}/\text{kg}$) in the initial soil sample (taken from the Moscow region) ($n = 3$; $P = 0.95$)

Me	Exchange	Carbonate	Fraction of elements bound with Mn oxides	Fraction of elements bound with Fe and Al oxides	Organic-sulfide	Total
Cd	9.4 ± 0.6	2.10 ± 0.2	1.10 ± 0.02	1.0 ± 0.1	1.02 ± 0.04	14.6
Cu	25.8 ± 0.8	22.9 ± 0.7	11.6 ± 1.1	20.7 ± 0.8	6.6 ± 0.5	87.0
Zn	61.5 ± 4.9	46.7 ± 2.3	43.1 ± 2.6	25.7 ± 1.5	24.5 ± 1.9	201
Pb	13.0 ± 0.5	6.12 ± 0.24	3.9 ± 0.2	4.8 ± 0.2	0.90 ± 0.04	28.6

Table 5. Results of determination of various heavy-metal species ($\mu\text{g}/\text{kg}$) in the silty, dusty, and sandy fractions of a soil sample (taken from the Moscow region) ($n = 3$; $P = 0.95$)

Me	Silty			Dusty			Sandy		
	exchange	carbonate	fraction of elements bound with Mn oxides	exchange	carbonate	fraction of elements bound with Mn oxides	exchange	carbonate	fraction of elements bound with Mn oxides
Cd	14.2 ± 0.8	5.5 ± 0.4	2.2 ± 0.1	11.9 ± 0.4	0.75 ± 0.02	0.75 ± 0.02	2.3 ± 0.1	0.20 ± 0.01	0.25 ± 0.01
Cu	35.3 ± 2.8	31.5 ± 1.9	20.3 ± 1.6	31.6 ± 1.9	29.9 ± 1.8	13.6 ± 0.7	8.4 ± 0.7	7.5 ± 0.5	0.98 ± 0.06
Zn	91.5 ± 6.4	80 ± 7	76 ± 4	86 ± 8	57.5 ± 5.2	52 ± 3	7.0 ± 0.4	2.6 ± 0.1	1.30 ± 0.02
Pb	25 ± 2	13.2 ± 0.8	8.5 ± 0.3	15.7 ± 0.9	4 ± 0.1	2.4 ± 0.2	1.20 ± 0.04	1.16 ± 0.07	1.00 ± 0.06

observed for all elements. The heavy-metal content increases in the following series: elements bound with manganese oxides, carbonate fraction, and exchange fraction.

Various element species in the silty and dusty fractions of the standard sample were also extracted in

RCCs. In this case, an equal distribution of heavy metals among the grain-size fractions was observed. As is evident from Table 6, the main part of Zn, Cu, and Pb is concentrated in the exchange form and is bound with manganese oxides. The carbonate form is poor in heavy metals.

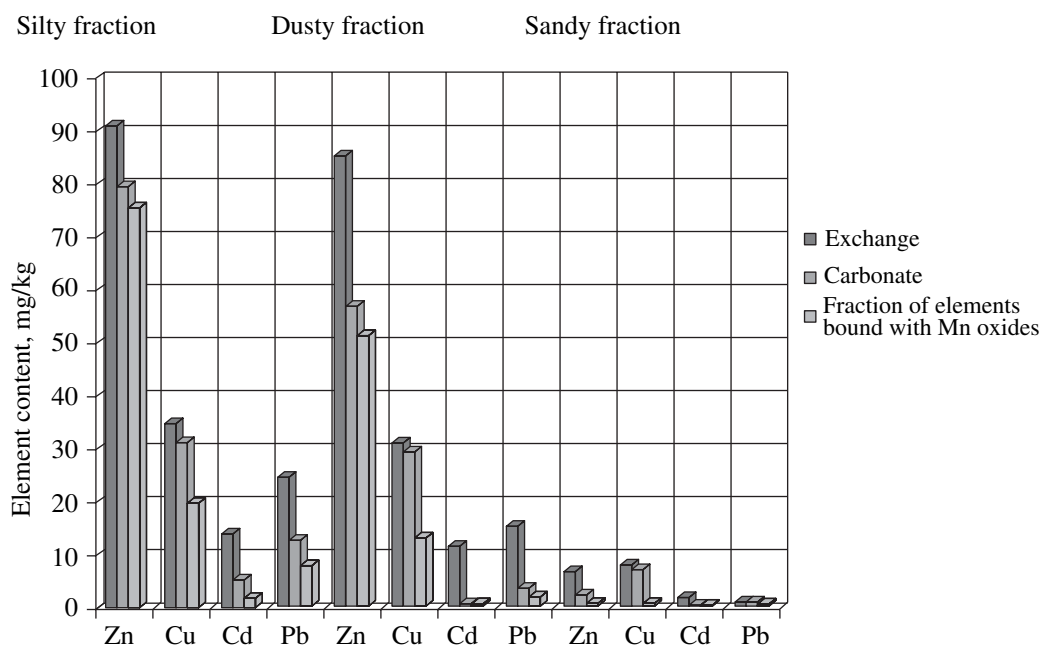
**Fig. 3.** Use of rotating coiled columns for the fractionation of soil particles and the sequential extraction of heavy-metal species from silty, dusty, and sandy fractions.

Table 6. Results of determination of various heavy-metal species ($\mu\text{g}/\text{kg}$) in the silty, dusty, and sandy fractions of a standard (SRM-2710) soil sample ($n = 3$; $P = 0.95$)

Me	Element content in the first three fractions, ($\mu\text{g}/\text{kg}$)	Silty			Dusty		
		exchange	carbonate	fraction of elements bound with Mn oxides	exchange	carbonate	fraction of elements bound with Mn oxides
Zn	2503 \pm 34	1036 \pm 12	615 \pm 4	820 \pm 9	1032 \pm 12	615 \pm 5	815 \pm 14
Pb	3928 \pm 67	1981 \pm 35	487 \pm 7	1428 \pm 16	1976 \pm 40	486 \pm 5	1420 \pm 14
Cd	19.3 \pm 0.3	15.0 \pm 0.3	1.7 \pm 0.1	2.4 \pm 0.1	14.8 \pm 0.3	1.6 \pm 0.1	2.2 \pm 0.2
Cu	2006 \pm 34	1060 \pm 17	253 \pm 4	665 \pm 16	1053 \pm 18	251 \pm 6	661 \pm 19

Thus, by the example of the determination of heavy-metal species in the initial samples of soil, it was demonstrated that manganese, iron, and aluminum oxides play an important part in the concentration of metals. The exchange form is the main heavy-metal species in the initial samples. It follows from the above that RCCs can be successfully used for the development of a complex method of studying the distribution of metal species in soil fractions differing in size and density in a sufficiently short period of time and with the least possible losses.

The determination of the content of various elements and their species in each fraction yields a detailed pattern of the distribution of elements and allows their lability, availability, and potential environmental danger to be evaluated.

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