



Information Resources of Soil Nanoparticles Chemistry

Panova Elena*

Saint-Petersburg State University,
Saint Petersburg, Russia

Oleynikova Galina

Saint-Petersburg State University,
Saint Petersburg, Russia

Abstract: The study's objectives were to develop a methodology for the isolation of soil nano-fraction (colloid-liquid phase) and determine the content of elements and study its distribution in the liquid phase and the soil samples. Nanofraction (colloid-salt fraction) is the part of a sample with a particle size less than 1000 nm. Nanofraction (NF) was isolated with deionized hot water from soil samples 30 g (soil: water - 1:10). The suspension was mixed for 6 h, settled for 24 h, and filtrated using a membrane filter ($<1 \mu\text{m}$). Mass spectrometry with inductively coupled plasma (75 elements) analyzed the soil sample and its Nano-Fraction. The chemical characteristics of the extracted liquid phase of the soil reflect its water-soluble component properties. Comparing the data obtained with the analysis results for the whole soil allows the assessment of a share of easily mobile and difficultly mobile forms of chemical compounds. This is the necessary basis for the development of a model describing the transport of metals in soil.

Keywords: Soil, nanoparticles, chemistry, agriculture

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I. INTRODUCTION

One of the fundamental problems of soil science is the determination of natural mechanisms responsible for the behavior of metals in the pedosphere, which is of natural and applied significance. The most important are studies of the behavior of mobile chemical elements capable of migration. Many specialists have shown that soil solutions played an important role in soil formation since all the processes of chemical and biological transformation of organic and mineral compounds proceed directly in the soil liquid phase. The solid phase of soil acts as an ion exchanger and carcass of the migration medium. One of the contemporary topical problems is the determination of the chemical composition of soil solution and its changes in the soil profile [1, 2, 3, 4]. Some concepts of molecular soil science, matrix and nanostructural organization of soils, are considered [5, 6, 7]. Despite the interactions between organomineral colloids and the surface of solid particles having been investigated since in the middle of the last century, it only became possible to reveal the fractal structure of soil organomineral gels and develop a

colloid chemical model of soil at present. [8, 9, 10].

The first attempts to isolate soil solution with water and its analysis were made by N.T de Saussure in the early nineteenth century. At present, the most common methods of obtaining the soil liquid phase are divided into three groups [11, 12, 13, 14]:

- methods with displacing liquid (water, salt, alcohol, acid, and other extracts (displacement of soil solutions with alcohol or other immiscible liquid));
- lysimetric methods (without application of pressure);
- methods using positive or negative pressure (pressing, centrifugation, extraction with gas under pressure, and vacuum-filtration).

Application of modern technique and methods of direct visual observation of nano-particles such as high energy transmission electron microscopy, high resolution scanning transmission electron microscopy with wave and dispersion spectrometer, tunnel scanning microscopy, atomic-force microscopy and others has allowed studying particles with size up to 0.25 nm. But the determina-

*Correspondence concerning this article should be addressed to Panova Elena, Saint-Petersburg State University, Saint Petersburg, Russia
E-mail: e.panova@spbu.ru

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tion of chemical composition of nano-particles has some difficulties. In the course of microprobe analysis due to the extra small size of nano-particles the probe burns through them and does not give the opportunity to evaluate their chemical composition independently from the matrix. Analytical sensitivity is 0.01% at the same time the local composition of single particles of the sample does not reflect the geochemical specificity of the whole rock. Thus, despite the developed general ideas of mobile and fixed forms of elements in soil and methods for their extraction, there is a lack of experimental quantitative data, which would allow for evaluation of the behavior of mobile forms of many macro- and microelements in the soil.

The objectives of the study were to develop a methodology for the isolation of soil nano-fraction (colloid-liquid phase) and determine the content of elements and to study its distribution in the liquid phase and the soil samples.

II. OBJECTS AND METHODS

The widespread type of soil on glaciolacustrine deposits in North-West Russia is the object under study: soddy-eluvial-metamorphic soil (Retic Albic Stagnosol (Clayic)) [15].

The soil on varved clays is formed under forest, and its profile is represented by the following horizons: O-AYg-ELg-BELg-BMg1-2-BC-C. The soil is characterized by the accumulative type of fulvate humus, acid reaction in the upper horizons, and well-pronounced eluvial distribution of clay. The texture of the eluvial (Yg, ELg, and BELg) and metamorphic (BMg1 and BM2) horizons differs from that of the parent rock by the lower content of clay fraction. Strong excessive moistening of the upper horizons and acidification of the soil result in the mobility of many elements with variable valence, especially iron and manganese. The determination of various iron and aluminum compounds in the soil using the Tamm method showed that in the ELg horizon, where the gley process is especially well pronounced, the content of mobile iron (mineral amorphous and weakly crystallized) was at maximum. The maximum content of mobile aluminum is also recorded in the eluvial horizons. The predominant clay minerals are dioctahedral illites and mixed-lattice clay minerals of the illitesmectite type; the participation of kaolinite and chlorite is limited. As a result of surface gleying, the mixed-lattice clay minerals accumulate in the upper horizons.

A method of analyzing the nano-fraction (water-soluble fraction) of soil. The first task for studying nanoparticles is the development of a method for its isolation nanoparticles solution from the soil (the separation

of the mineral matrix). In addition, the methodological methods for the registration of a great number of metals should be improved to achieve their detection at such low concentrations. The development of a method for the isolation of soil solution is based on principles of extraction of pore water (soil, rocks, silt). Some relevant approaches were taken from the geochemical methods of studying the mobile forms of chemical elements that were earlier proposed.

As a basis for the method of separation of particles with the size, less than $1\mu\text{km}$ is taken the fact that under special conditions nano-particles can form in water colloid solutions which are stable for a long time. It is possible to separate colloid particles from water only using different coagulants or by means of ultra centrifugation. The appliance of filters with pores $1\mu\text{km}$ for filtration allows to adhere to the upper particle size: all the particles in the solution are of nano size - up to $1\mu\text{km}$. The bulk of substance in the analyzed solution is determined by weighing method having evaporated water from the aliquot sample of the solution. It was suggested to call this fraction nano-dispersed or nano-fraction (NF) [16].

Method of separation and analysis of nano-fraction worked out by the authors is covered by patents of RF (№2370764 from 20.10.09). It suggests water treatment of soils samples under special conditions which ensure to reduce completely into solution all forms of chemical elements with the size up to $1\mu\text{km}$. Particles with the size more than $1\mu\text{km}$ are removed by filtration through a porous filter, at this in the solution there remain colloid particles and the substance in ionic form (soluble salts). Analysis of NF solutions was carried out by ICP MS method at « ELAN-6100 DRC », PERKIN ELMER.

The carried out experiments on separation of soil NF have demonstrated that its amount is - 0.5-6 wt.%. Complete analysis of rock-forming oxides and micro-elements in NF has demonstrated that rock-forming components make up 90 wt %, which is quite obvious, and micro-elements constitute not more than 10 wt %. Calculations of chemical elements concentrations were carried out both in NF and in the soil sample from which it had been separated. Samples of soils and their NF have been analyzed for 75 elements. It is necessary to point out, that analysis of water solutions allow to realize the possibilities of ICP MS method at most, because there is no negative influence of additional chemical reagents which in its turn results in lowering the detection limits of rare and trace elements in initial samples in 2-3 orders. The detection limits are (soil/NF, mg/kg): U-0.01/0.00002; Tl-0.03/0.00006; Mo-1.0/0.0002; Cd-0.1/0.0006; Hg-0.005/0.0005; Se-0.5/0.01, Te-1.0/0.002; Sb-0.1/0.0006; Bi-0.2/0.0001;

As-0.6/0.001; Zn-1/0.01; Ni-1/0.05; 0.5/0.01 (Co); 1/0.05 (Cu); 1/0.05 (Pb); In-0.01/0.0002; 0.04/0.0004 (Pt), 0.03/0.0006 (Pd), Au-0.002/0.0002; Ag-0.05/0.0001; Re-0.03/0.0001; Sc-0.1/0.0006; Ge- 0.03/0.0006; Ga-0.05/0.0002; Sc- 0.15/0.0006; In-0.01/0.0002; etc.

III. RESULTS AND DISCUSSION

Concentrations of chemical elements in the NF and in the whole soil samples, from which it was isolated, are

presented in Table 1, Table 2. Tables demonstrate significant differences in the total content of chemical elements in the soil and in its NF, which is characteristic of both macro- and microelements. Studies have shown the presence of a high proportion of mobile (water-soluble) forms of elements. In different horizons of soil profile, the ratio of mobile and fixed forms is different. The largest share of mobile forms is marked in the horizon B1g BM2.

TABLE 1
MACRO ELEMENTS IN THE CLAYEY SOIL, PROFILE AND ITS NANOFRACTION (%)

Soil Profile	SiO_2		TiO_2		Al_2O_3		Fe_2O_3		MnO	
	Soil	NF	Soil	NF	Soil	NF	Soil	NF	Soil	NF
AYg	72.5	0.14	0.81	0.035	12.74	0.33	5.65	0.48	0.17	0.14
Elg	73.5	0.42	0.67	0.39	11.01	4.15	4.75	4.38	0.11	0.22
B1g	70.1	1	0.74	1.04	15.31	12.1	6.15	8.16	0.09	0.13
BM2	65.2	1.01	0.68	1.02	13.11	11.3	5.17	8.92	0.07	0.12
BC	65	1	0.79	1.04	14.68	10.8	6.08	8.2	0.09	0.12
C	64.9	0.98	0.84	0.74	16.46	9.97	7.18	6.77	0.08	0.071

Soil Profile	CaO		MgO		Na_2O		K_2O		P_2O_5	
	Soil	NF	Soil	NF	Soil	NF	Soil	NF	Soil	NF
AYg	1.24	2.22	1.08	0.8	1.09	0.25	3.11	0.22	0.16	0.045
Elg	0.97	1.61	0.73	0.82	1.22	0.47	2.91	0.4	0.13	0.099
B1g	0.99	1.24	1.92	2.25	1.12	0.69	3.37	1.05	0.13	0.1
BM2	1.13	1.48	1.32	2.19	1.18	0.77	3.07	0.99	0.12	0.13
BC	1.13	1.35	1.69	2.27	1.13	1.02	3.28	0.96	0.14	0.11
C	1.15	1.15	2.18	2.21	1.01	0.79	3.51	0.91	0.14	0.09

TABLE 2
MICRO ELEMENTS IN THE CLAYEY SOIL PROFILE AND ITS NANOFRACTION (MG/KG)

Soil Profile	Be		Sc		Ga		Ge		V		Ag	
	Soil	NF	Soil	NF	Soil	NF	Soil	NF	Soil	NF	Soil	NF
AYg	1.79	0.21	11.8	15.7	17.1	0.8	1.84	0.085	97.3	8.2	0.94	0.8
Elg	1.4	0.83	10.1	74	13.7	9.34	1.87	0.96	72.6	67.1	0.8	3.1
B1g	2.83	2.6	14.7	150	20.1	25.4	1.89	2.62	97.9	133	0.85	8.86
BM2	2.39	2.7	13.2	146	16.5	25.8	1.88	2.49	95.8	137	0.82	8.46
BC	2.98	2.63	14.5	132	19.9	23.3	1.86	2.05	109	134	0.86	9.52
C	3.53	2.47	16.7	107	22.9	21.4	2.09	1.64	138	113	1.05	6.82

Soil Profile	Co		Ni		Cu		Zn		Mo		Cd	
	Soil	NF	Soil	NF	Soil	NF	Soil	NF	Soil	NF	Soil	NF
AYg	21.6	3.05	27.6	4.01	16.6	5.91	84.9	191	1.56	2.05	0.12	0.054
Elg	12.9	15.4	22.7	14.1	11.6	12.8	60.6	538	0.96	1.23	0.15	0.08
B1g	22	25.4	70	42.4	38.1	62.9	109	422	2.67	2	0.26	0.11
BM2	15.2	19.7	34.2	49.2	33.2	90.2	61.9	246	1.08	4.82	0.19	0.21
BC	17.7	18.5	62.3	60.6	34.5	66.6	70.3	437	1.07	2.61	0.17	0.3
C	19.2	14	48.5	42.7	34.2	46.9	83.4	313	0.88	1.91	0.13	0.13

TABLE 2 CONTINUEE..

Soil Profile	Sb		Pb		Y		ΣREE		Th		U	
	Soil	NF	Soil	NF	Soil	NF	Soil	NF	Soil	NF	Soil	NF
AYg	0.41	0.21		2.5	20.9	1.05	157.26	6.67	11.2	0.67	2.92	0.48
Elg	0.32	0.36	21.8	13.8	20.4	4.88	144.14	66.04	10.6	5.39	2.9	1.54
BMlg	0.51	0.64	23.4	22.3	28.2	25.3	213.13	272.67	14.3	17.9	3.91	4.87
BM2	0.46	1	25.4	45.8	33.9	38.6	220.08	354.68	13.9	23.2	5.7	10.1
BC	0.62	0.6	23.3	23.7	34.1	35	224.87	326.74	14.2	20.8	5,07	7,91
C	0.42	0.51	19.8	17.6	33.8	23	249.70	233.04	15.6	15.5	4.27	3.98

Soil Profile	Ba		Rb		Sr		Cr		Zr		Nb	
	Soil	NF	Soil	NF	Soil	NF	Soil	NF	Soil	NF	Soil	NF
AYg	560	193	136	8.57	131	85.3	89.6	9.47	304	4.27	18.3	1,15
Elg	550	432	121	62.7	137	54.5	81.5	38.2	330	52.1	14,4	12
BMlg	565	783	146	135	132	122	170	102	263	168	16	34.5
BM2	543	459	119	118	140	130	93.8	106	316	190	13.8	34.2
BC	558	979	140	119	136	150	137	94.2	253	203	16.7	37.4
C	546	645	158	113	129	114	128	84	228	137	18.1	24.3

In the clayey soil, the share of fixed forms of macro- and microelements was high; A high migration capacity was observed for microelements (Sc, Ag, Zn, Mo, Cu, Sb, Ge, Ga).

The values showing the weight share of the water extract characterizing the NF of the soils are given in Table 3. In the soil profile, the NF share increased from the AY horizon to eluvial or podzolic horizons, then decreased, and again increased in the deeper ones. When calculating the content of elements in the NF on the total soil mass, a tendency of the depletion of the soil in mobile elements compared to the parent rock was re-

vealed. In the clayey soil Sc is mainly present in the mobile form, the maximum contents in NF were confined to the BC and C horizons. In the EL horizon, the mobility of some elements was higher as compared to that in the humus horizon. The metamorphic horizons (BMg1 and BM2) were characterized by the widest spectrum of water-soluble elements. The removal of Fe, Al, Ti, and K and many other elements (the data of the total chemical analysis) from the soil on the background of the relative accumulation of Si and REE showed that these horizons could not be qualified to be alluvial.

TABLE 3
PART OF NANOFRACTION IN THE SOIL SAMPLE (WT %)

Soil horizon	NF, wt %
AYg	0.63
Elg	0.98
BMlg	0.84
BM2	0.83
BC	1.28
C	1.65

Probably, the metamorphic process promoted the weakening of crystalline lattice in minerals, resulting in the increase of the potential mobility of many elements. In the iron illuvial horizons, the degree of mobility of most elements decreased, which was also characteristic of the BC horizon close to the parent rock (C) in terms of chemical composition. According to the composition of water-soluble elements, the BC of the clayey soil is closer

to the middle horizons of the soil profile than to the rock, where the share of mobile forms decreases.

IV. CONCLUSION

(1) A method for the isolation of the nano-fraction for analyzing the mobility of chemical elements is suggested. The analysis of water solutions without decomposition of soil and addition of reagents allows maximizing the

opportunities of mass spectrometry with inductively coupled plasma (to lower the detection level for rare and scattered metals, to increase the spectrum of elements, and to get reliable information at their super-low concentrations), which makes it possible to raise significantly the information capacity of soilchemical studies.

(2) The portions of easily and difficultly mobile forms of elements were evaluated for widespread soil in the Russian Plain. Significant differences in the total content of chemical elements (based on the total chemical analysis) in the soils and their NF (water-soluble fraction), as well as in the composition of this fraction in the clayey soil, were revealed.

(3) The regularities of the distribution of chemical elements in the nano-fraction of the soil studied correspond in many aspects to the revealed regularities in the behavior of chemical elements in the course of soil formation. Particularly, the upper part of the profile of the clayey soil is shown to be a zone of eluviation impoverished in most elements. In the lower part of this profile, the removal of elements becomes weaker, which is characteristic of the eluvial processes.

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