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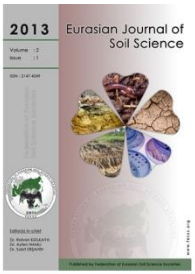

Pedotransfer capacity of nickel and platinum nanoparticles in Albeluvisols Haplic in the South-East of the Western Siberia

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Abstract

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Findings of field and experimental studies of pedotransfer capability of nickel and platinum nanoparticles in the profile of Albeluvisols Haplic of the sub-boreal forest in the south-east of the Western Siberia were presented. Results of the surveys testify to the effect that major factors affecting the migration capability include large biogenic interstices and main cracks that act as transport channels for nanoparticles, as well as thermodynamic (φ-) potentials of particles that define the intensity of surface electrostatic interactions with walls of soil interstices.

Keywords: nickel and platinum nanoparticles, soil, migration, physical properties

Introduction

Before long, the onrush of nanotech industry can lead to the emergence of a new type of xenobiotics – inert particles smaller 100 nm resistant to environment and capable of accumulating in plants and living organisms having various effect, including toxic.

Soil – is a main depot of pollutants in ecosystems, an initial link of water-migration ways and trophic chains. The creation of a theory of nanoparticles behavior in soils will allow not only foreseeing emerging effects, but also creating the technology of remediation.

So far, many works have been published concerning nanoparticles transfer through porous media, including soils, however in most cases the expression "nanoparticles" is used as a semantic equivalent to soil colloids. Most often, synthetic porous media with established "idealized" parameters are used. Sometimes nanoparticles mean all grain-size fractions of a small diameter, as in the work of Li et al. (2010).

In this work nanoparticles mean particles of anthropogenic origin only. In a number of works (Duester et al., 2011; Fanga et al., 2009; Kovenya et al., 1972) and others, they show that nanoparticles have a high potential to migration in porous saturated media. Soil is attributed to them too. That is why nanoparticles are referred to a category of potentially dangerous substances that can spread to substantial distances from a source of pollution. However not all nanoparticles are capable of far migration, as illustrated by Jaisi and Elimelech (2009), a number of nanotubes have good sorptive affinity with soil matrix and are not dangerous pollutant in migration terms.

Particles of such a small diameter are permanent for soils, and the diameter itself is not their distinctive feature. The specified dimensional class in soils includes varied components of loamy organic-mineral matrix (soil nanoparticles): fractures of primary minerals and secondary loamy minerals; organic-ferrous, organic-loamy, and organic-mineral colloids; organic substance, etc. However, all these components are

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often immobile and due to high surface charges they form structures of complex geometry (ensembles): quite large structures, separate domains of which can be about 1 mcm, and ensembles themselves having high strength provide for water resistance of soil aggregates. That is why anthropogenic nanoparticles of inert metals will differ significantly from surface particle of similar dimensions in terms of their properties. This article shows the behavior of nickel and platinum nanoparticles less than 50 nm.

In 2008, in Tomsk town, the first block of the Technical and Innovation Zone was brought into operation. It initiated the formation of Tomsk innovation cluster. The cluster included enterprises where nanotechnologies were applied, thus a threat of emerging of a new type of pollutants – nanoparticles – appeared. In this regard, an experiment of pedotransfer capacity of nickel and platinum nanoparticles was conducted at Albeluvisols Haplic (according to the Russian classification – sod-podzol soil), because this component of the soil covering was the leading one in the sub-boreal forest of south-east of the Western Siberia and surroundings of production spaces of Tomsk technical and innovation zone, in particular.

Material and Methods

The experiment to study the migration of nanoparticles was conducted in the field environment. The section characterizing Albeluvisols Haplic was laid in the inter-crown space of the grassland birch forest in the eluvial position on the second above the flood plain terrace of the Tom river. The profile formula (strength, cm): A (0–11/14) – AE (11/14–30/34) – E (30/34–57/60) – EB (57/60–83) – Bt (83–100/110) – Bt–BC (100/110–140) – BC (135 – 190/200) – C˜ (190/200 – 240+). The following was identified in the surface: the sum of exchangeable bases; absorbed calcium and magnesium; the content of humus according to Tyurin (wet oxidation); hydrolytic acidity; active acidity; full and capillary water-absorbing capacity; solid phase density; general porosity (Vadyunina and Korchagin, 1986). To determine the content of nanoparticles in experimental samples and source solutions, a mass spectrometry method with the ionization in the inductively coupled plazma was used. The sample preparation was carried out in the following way. They took samples of 0.10 g on analytic balance that were placed into a fluoroplastic cylinder (PTFE), added 0.2 – 1.0 ml of concentrated nitric acid, covered with a protective laboratory film and put it into a thermal unit heated up to 115 °C, kept it during 0.5 – 1.0 h until complete dissolution of the sample. The dissolved sample was quantitatively transferred into a measuring polypropylene test tube washing off the cylinder walls three times, and brought with the deionized water up to 10 ml. They closed it pressure-tight with a protective laboratory film, mixed and analyzed it using a mass spectrometer “ELAN DRC-e” model.

The studied section was a control variant to select samples from experimental plots, where the suspension of nickel and platinum nanoparticles was introduced. To avoid the influence of space variation of soil capacities on the experiment, test points were placed in the distance about 3-4 meters from the control section.

In test points the suspension of nanoparticles was introduced according to a standard method of small covered areas to study filtration properties of soils. An internal round frame of the diameter 20 cm and an external frame of the diameter 40 cm was put on the soil surface. During the suspension introduction, a constant water column was supported over the soil surface 5 cm high to provide the flow stability and the drenching speed, as well as the flow rate. The suspension was introduced into the internal ring with some delay to have the horizontal moisture edge of the external frame go down earlier than the suspension inside the ring. That enabled to minimize the side outflow of nanoparticles suspension. The concentration of the nanoparticles suspensions was selected based on the lowest speed of sedimentation in the concentrations range. 10 mg/l for platinum and 40 mg/l for nickel was selected as the most suitable suspension concentration. The suspension volume was 10 liters (based on the annual standard of soil drenching that made around 300 l/m^2). The suspension was introduced in 2 promptitudes for each test material.

After absorption and finishing of the suspension filtration in 2 days, samples were selected by the column from the following depth range: 0–5; 5–10; 10–15; 15–20; 20–25; 25–35; 35–45; 45–55 cm. Using the method that provides for the randomness, average samples were selected from obtained samples (control and two replications for every metal under study) that were further studied in terms of the substance content that composed required nanoparticles.

Table 1. Physical-Chemical and Physical Properties of Haplic Albeluvisol

Horizon	**Sampling depth, cm**	**CEC, cmol(+).kg^{-1}**	**Ca^{2+}, cmol(+).kg^{-1}**	**C org, %**	**Hydrolytic acidity, cmol(+).kg–1**	**Base saturation SAC, %**	**pH**	**Maximum water holding capacity, %**	**Capillary water holding capacity, %**	**Particle density, g/cm^3**	**Build density, g/cm^3**	**Humidity during experiment, %**	**General porosity, %**
A	0–8	16,4	13,6	5,6	5,3	76	6,4	74	73	2,4	0,80	29	67
AE	10–20	7,6	5,2	1,5	5,6	58	5,3	37	29	2,6	1,29	17	50
E1	22–32	4,4	3,6	0,4	3,2	58	5,1	26	23	2,6	1,46	11	44
E2	40–50	5,2	4,8	0,4	3,3	61	5,1	27	25	2,6	1,48	10	43
EB	60–70	7,2	6,4	0,4	3,2	69	5,3	29	26	2,7	1,55	14	44
Bt	90–100	12,8	9,6	0,3	3,5	79	5,4	34	30	2,8	1,58	16	43
Bt	115–125	11,2	8,8	0,2	2,6	81	5,7	34	30	2,8	1,57	16	44

Table 2. Grain-Size Composition of Haplic Albeluvisol

Horizon	**Sampling depth, cm**	**Fraction diameter, mm, content, %**							**Name according to the Russian classification of N.A. Kachinsky,**
		1-0,25	**0,25-0,05**	**0,05-0,01**	**0,01-0,005**	**0,005-0,001**	**<0,001**	**Physical clay (<0,01)**	
A	0–8	23	37	26	4	2	6	12	coarse silt - fine sand sandy loam
AE	10–20	23	34	25	5	4	8	17	coarse silt - fine sand sandy loam
E1	22–32	28	33	23	3	4	8	15	coarse sand - fine sand sandy loam
E2	40–50	27	32	22	3	2	10	17	coarse sand - fine sand sandy loam
EB	60–70	25	33	20	4	1	15	20	coarse sand - fine sand sandy loam
Bt	90–100	13	32	29	2	4	20	25	coarse silt – fine sand light loam
Bt	115–125	38	30	8	3	4	16	22	fine sand – coarse silt light loam

Results and Discussion

The peculiarity of the studied Haplic Albeluvisol is the presence of a gradient and stretched transition between genetic eluvial E and texture Bt horizons in the form of sub-eluvial horizon EB. The height of the transition zone is 20-35 cm. Together with this transition, properties change, the composition of density and the quantity of silt fractions increase along the profile – it is a reflection of conditions of their formation (Loyko et al, 2011). The studied soil, being light grain-size, has quite low pH values and exchangeable bases characteristic for such soils of the forest zone, except for the organogenic horizon AY, where these values increase for the account of biologic accumulation of bases on the matrix of an organic substance (Table 1).

The whole profile differs by the average degree of saturation with bases, with the lowest values in eluvial (EL) horizons - 59–60 %, and in humus and texture horizons values approximate to 80%. Taking this into consideration, we can assume that during the profile wash-out with the nanoparticles suspension prepared using the distilled water for the account of exchangeable reactions, the solution chemical quality change will not occur significantly or quickly that could affect the nanoparticles aggregation speed. The biggest content of bases is observed in the humus horizon, however it has the minimum composition density with the maximum porosity; due to that reason, the introduced solution will come through this horizon quite quickly (the water penetration speed approximately 26 cm/h), and the time will not suffice for exchange reactions to occur.

Generally, we can note the presence of three horizontal sections inside the profile, where the moisture movement conditions change occurs. This is a lower part of the humus horizon, where the break of multiple capillaries is observed, and the general porosity decreases. The second zone is located under the lower part of the humus-eluvial horizon (AE), where the porosity decreases, and the composition density increases, and the third zone on the border of the illuvial horizon, where the differential porosity changes due to the abrupt change of the grain-size composition (Tables 1 and 2). According to Syso (2007), the gross content of Ni in soils of the Western Siberia is within the range from 20 to 65 mg/kg. As a rule, the content of nickel in soil-forming rocks is higher than in soil horizons, i.e. its desalination occurs. In the control variant of the soil under study the content of Ni has the accumulative-eluvial-illuvial type of distribution. The maximum falls on the humus-accumulative horizon, then the composition decreases, and its quantity increases again nearer to illuvial horizons (Table 3). Such nickel distribution can indicate its anthropogenic introduction into the soil together with precipitations, because the survey territory is located in the natural condition, but within the town boundaries.

Table 3. Nickel and Platinum Content in Samples

Sampling depth, cm	Control		Experiment data (2 replications)		Nanoparticles concentration in a layer		Layer-by-layer accumulation	
	Ni	Pt	Ni	Pt	Ni	Pt	Ni	Pt
	mg/kg						mg	
0–5	24,2	<0,01	76,3	0,30	52,1	0,30	65	0,38
5–10	20,0	<0,01	22,5	4,00	2,5	4,00	3	5,02
10–15	18,8	<0,01	18,8	1,73	0,0	1,73	0	3,42
15–20	16,9	<0,01	20,4	0,87	3,5	0,87	7	1,80
20–25	13,2	<0,01	21,1	0.53	7,9	0,53	18	1,17
25–35	14,5	<0,01	75,6	0,48	61,1	0,48	278	2,20
35–45	14,2	<0,01	19,9	0,34	5,7	0,34	26	1,58
45–55	18,8	<0,01	19,3	11.34	0,5	11,34	3	55,19

The platinum content is negligibly small that does not allow the identification of its changeability within the profile. Besides the concentration, the Table 3 shows the values of difference of concentrations and layer-by-layer accumulation. The concentration of nanoparticles in a layer – is a value obtained during subtraction of the control samples element concentration from test points. The layer-by-layer accumulation shows the metal accumulation in a cylindrical layer with 20 cm section (the composition density is taken into account). The layer-by-layer accumulation is calculated according to the formula: ПА=Псл×Vсл×Кнч/1000, where ПА – layer-by-layer accumulation; Псл – layer composition density (g/cm^3); Vсл – layer volume; Кнч – nanoparticles concentration in a layer (the difference between the control and test). The distribution of nanoparticles in the profile of two metals has a complex nature. At the same time, the distribution of platinum repeats in the first approximation the change of the composition density in the profile, or rather maximums of its content are confined to areas of the largest vertical density gradient, or the weighting of the grain-size composition and the general porosity change. In every such case one can assume the changing of the porous space geometry and deterioration of the radial migration conditions. The platinum accumulation points indicate places, where the substance inflow values exceed its outflow. The first maximum of the platinum accumulation (Table 3, Figure 1) lies within the range of 5-15 cm, when friable fine-grain-powdery cespitose horizon transfers into fine-grain-crumbly eluvial-humus horizon, and together with that a sudden change of density value and general porosity decreasing (for the account of biogenic pores) occurs.

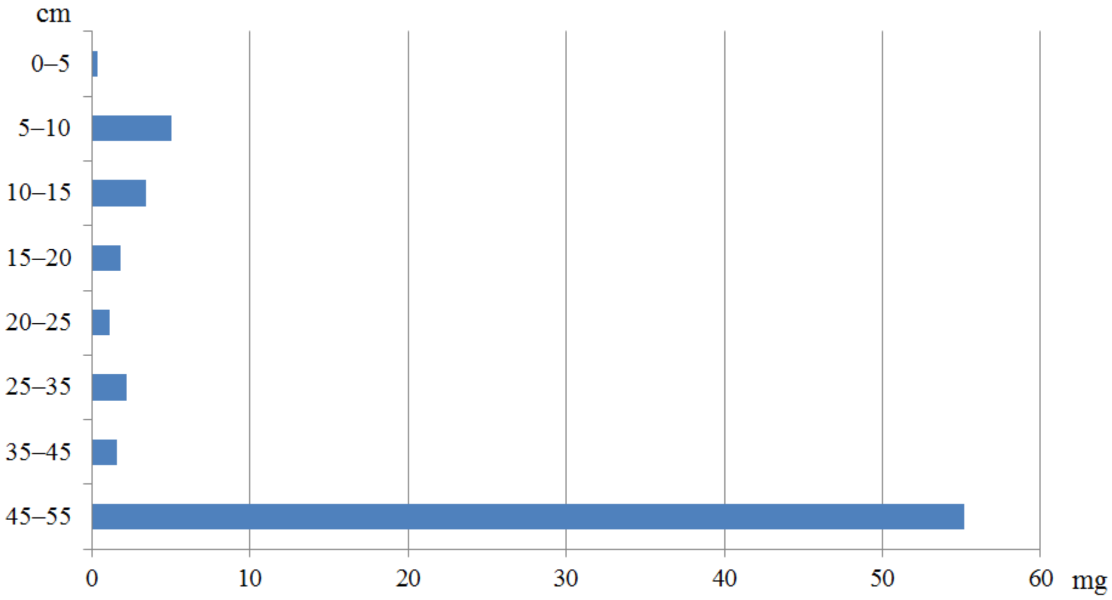

Figure 1. Layer-by-layer accumulation of platinum along the profile Haplic Albeluvisol after the experiment.

The following peak is confined to the lower border of EL horizon, i.e. conditioned by the influence of the water-resistant texture horizon that slows down the flow of the infiltrating moisture abruptly from one side, thus making platinum nanoparticles coagulate and subside, and from another side, decreasing of the pores diameter can mechanically detain the migrating platinum nanoparticles, though this mechanism is hardly probable, because the size of nanoparticles should provide for their penetration into any pore, where the moisture transfer is possible. That is why, one can assume that the accumulation of platinum nanoparticles occurs mechanically and is connected almost fully with the correlation of the moisture migration speed and the platinum sedimentation speed.

It is hard to assume for the inert platinum the possibility of acquiring a charge as a result of partial surface dissolution that is why the electrostatic interaction of platinum nanoparticles with the soil absorbing complex and electrolytes of soil solutions is practically excluded, at least, in short periods of contact, when the experiment was conducted. The profile distribution of nickel nanoparticles (Table 3, Figure 2) has a bimodal nature.

However, the first maximum is in the layer of the humus horizon already. The higher location of the first accumulation peak makes it possible to assume a somewhat another mechanism of binding. Thus, during the suspension preparation, the aggregation and sedimentation of nickel nanoparticles was observed, comparing to platinum. It indicates indirectly that nickel nanoparticles obtain the surface charge on the stage of working suspensions preparation. That is why, getting into the humus horizon of higher absorption capacity caused by hydrophilic humus acids (5.6% of the content (Table 1)), nickel nanoparticles start intensive absorption in active centers of organic substance molecules, forming electrostatic associations with the latter. A large number of plant residues can be found at this depth that lost their anatomic structure and partially humified, but at the same time preserving the carcass structure with the formation of fiber structures, with a large number of twisting and one-side open pores that can mechanically detain nickel nanoparticles effectively. Some quantity of nanoparticles that go along large pores migrates into lower soil layers. By that time, the larger part of nickel nanoparticles aggregates it that is why in the second zone (under the lower part of the humus-eluvial horizon (AEL)) of the nanoparticles migration deterioration practically complete sedimentation of nickel nanoparticles occurs. The reason for that are not electrostatic effects, but the loss of filtration speed during the porosity reduction in the vertical direction with the parallel increasing of the composition density.

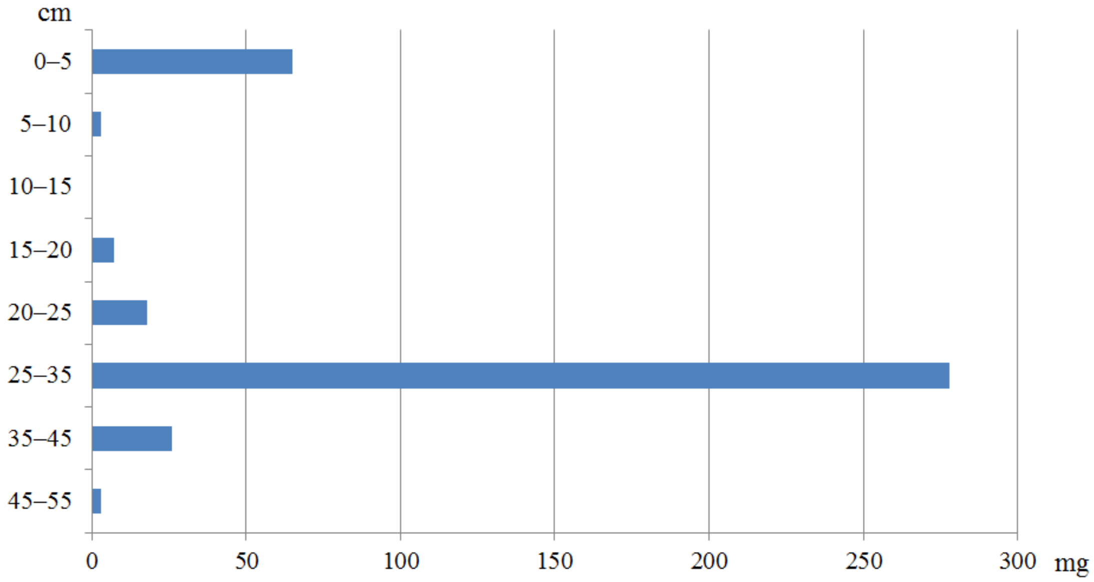

Figure 2. Nickel layer-by-layer accumulation along Haplic Albeluvisol profile after the experiment.

Some assumptions can be made by the summation of layer-by-layer accumulation values for each layer – it gives the value of nanoparticles composition after the experiment in the whole cylinder. These values for nickel are 400 mg, and for platinum – 71 mg. Taking into consideration that the source concentration of nickel solution was 40 mg/l, we can say that practically all nickel was detained in the test point cylinder. And the quantity of the introduced platinum was 100 mg; that is why we can say that 29 mg of platinum continued the migration into the depth of the soil profile, beyond 55 cm of strata.

It follows from above that the larger role during the determination of transfer capacities is played by the material inertness degree. Nanoparticles consist of this material. The less inert nickel, obtaining the charge, aggregates faster, interacts with soil colloids, as a result it subsides within the first 50 cm from the soil surface binding in the upper part mainly with the organic substance, and lower during the transition from the horizon AY to the horizon EL with the abrupt decreasing of the average weighted diameter of pores. Platinum nanoparticles are very inert, they have small surface charges and subside mainly on mechanic geochemical barriers, that is why their distribution in the profile is better harmonized with physical properties (porosity, composition density, grain-size content).

In total, it is noted that due to their finest size and super-disperse condition, nanoparticles showed a phenomenal migration capability in soils for colloid particles. It allows considering them as quite a dangerous type of pollutants capable of free and quick penetration inside the soil profile. On another hand, this peculiarity can be used for their elimination from the root layer by means of soils washing with water.

Conclusion

As a result of experiments conducted, it was established that platinum nanoparticles had higher migration potential as compared to nickel nanoparticles that can be connected with their high inertness and, therefore, the lesser thermodynamic (φ-) potential. Due to that, the platinum comes into electrostatic interactions with soil pores' walls with less intensity, and is aggregated in suspensions weaker than nickel.

When studied nanoparticles come into the soil profile, their primary accumulation occurs in the upper root layer, but their part comes beyond its borders, which is especially characteristic for platinum, the carryover of which can make about 20-30% with a single drenching from the initial content.

It is shown that the leading role is played by biogenic pores and main cracks, where nanoparticles are transported quickly into the depth of the profile, without managing to aggregate and/or come into the electrostatic interaction with the surface of the porous space. The detention of nanoparticles occurs mainly mechanically, but with the growth of their surface charge the bigger part is played by the electrostatic interactions and coagulation effects caused by the interaction of soil electrolytes.

Nanoparticles that penetrated into the surface soil layers, provided their inclusion into the flow of side internal soil, soil-rock and rock waters can distribute to quite large distances resulting in the pollution of underlying catena soils and bodies of water. The approximate distribution distance in conditions facilitating the migration can make the first hundreds of meters, and the percent of nanomaterial that remained in the unbound condition can reach from 10% during the passing of horizons with the dense packing of aggregates, up to 60-80% with the high porosity (sands, pebbles, slope soils with a large number of flow tubes). At the same time, one should not assume a significant radial-lateral migration of nanoparticles in brackish and weakly aggregated soils of hard grain-size composition that should be taken into consideration during the pollution subsequences forecasting.

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