Composition of organic-mineral complexes (OMC) migrating in the reclaimed sod-podzolic soils (Umbric Albeluvisol Abruptic)

A V Litvinovich¹, O Yu Pavlova¹, A V Lavrishchev^{2,*}, and A A Belimov³

¹Agrophysical Research Institute, Grazhdanskiy pr., 14, 195220 St. Petersburg, Russia

²St. Petersburg State Agrarian University, Petersburgskoe shosse, 2, 196601 St. Petersburg, Pushkin, Russia

³All-Russia Research Institute of Agricultural Microbiology, Podbelsky shosse, 3, 196608 St. Petersburg, Pushkin, Russia

Abstract. The composition of organo-mineral complexes (OMC) migrating from the arable horizon limed by *Umbric Albeluvisol Abruptic* was studied. The carbon content in organic-mineral complexes (OMC) ranged from 5.5 to 5.7%. The optical density index ($E_s^{\text{mg/ml}}$) varied in the range of values from 2.7 to 3.1, characteristic for fulvic acids (FA). It was established that FAs averaged with bases retain the ability to exert a destructive effect on soil minerals, transferring a significant amount of Al, Mn, and Fe into solution. According to their ability to migrate as part of OMC, the elements studied in the experiment with dolomite particles at a dose of 7.35 t/ha were arranged in the following decreasing sequence: Mn > Al > Fe. In the experiment with conversion chalk (CC) at a dose of 20.25 t/ha, this sequence was Al > Mn > Fe.

1 Introduction

Water-soluble organic substances (WOS) are able to form stable compounds of complex nature with aluminum, manganese, and iron ions [1-5]. There is a close correlation between soil acidity and the mobilization of aluminum and iron from the crystal lattice of minerals [6-7].

The main role in the migration processes occurring in *Umbric Albeluvisol Abruptic* belongs to compounds of fulvic acid nature, which are actively involved in the movement of aluminum, manganese and iron in their profile.

With an excess of bases in the soil solution and bringing the latter to an alkaline reaction ($\text{pH} > 10$), OMC with FA-1 precipitate [8]. The scale of migration of the Ca, Mg, and Sr bases in the OMC of the reclaimed screening dolomite *Umbric Albeluvisol Abruptic* is quite significant [9].

With increasing pH of the soil solution due to liming, the cation-exchange capacity (CEC) of soil also increases. In the experiments [10] with a single application of 1Ng of lime due to the involvement of weakly acidic soil organic substances (OS) in the exchange

* Corresponding author: av.lavrishchev@yandex.ru

processes in the composition of humic acids, more and more reactive groups can be activated, which were previously blocked by internal chemical bonds or could not be activated at lower pH values of solutions, the cation-exchange capacity increased by 10-15%. As a result of liming, the CEC can increase up to 48% with periodic liming of 1Ng to 23-29% according to the authors.

This creates an opportunity for the interaction of the “free” functional groups of humic acids of the lime soils with other typomorphic elements (Al, Mn, Fe).

Studies aimed at establishing the mobility of aluminum, manganese, and iron as part of the OMC of soils limed by industrial waste are unknown to us.

The purpose of the research was to establish the extent of migration of Al, Mn, and Fe as part of the OMC Umbric Albeluvisol Abruptic, reclaimed by industrial waste, in laboratory experiments on columns.

Research Objectives:

- establish the carbon content in OMC removed during washing of lime soils;
- determine the optical density of the OMC solutions that precipitate when the pH of the eluates is adjusted to 13 units;
- to conduct a ranking of typomorphic elements according to their ability to join compounds with WOS, migrating in reclaimed soils.

2 Materials and methods

Two laboratory experiments were performed. Samples of reclaimed soils were taken from plots of the microfield experiment (experiment No. 1) and vessels of the vegetation experiment (experiment No. 2). They were dried, ground, sifted through a sieve with 1 mm holes and placed in polyethylene columns with a diameter of 65 mm. The mass of soil in the column was 800 g. The height of the soil layer was 18 cm. The packing density was 1.0-1.1 g/cm³. Repeat was 6-fold. The soil in the columns was saturated with deionized water to the first drop of leaked moisture. Then, washing was performed using 400 ml of water. After washing, the filtrate was collected in a flask.

0.1 N NaOH was added to the eluates, adjusting the pH to 13 units. Upon reaching the specified pH value, brown OMC flakes precipitated, which were separated from the supernatant, dried and analyzed, setting the content of Corg, $E_s^{mg/ml}$ and the presence of Al, Mn and Fe.

Soil samples for experiment No. 1 were taken from the plots of the microfield experiment one year after liming after harvesting peas (*Pisum sativum*). The experience was laid in 2015 to study the reclamation properties of the screening of dolomite used for road construction. The particle size of dolomite was 5-7 and 7-10 mm. The research methodology is described in detail in the works [11-12]. Repeat was 4-fold. The experimental scheme is shown in Table. 1. The dose of the reclamation agent is calculated by hydrolytic acidity of 7.35 t/ha. For comparison, dolomite flour (DF) was used, prepared from the screenings passed through a sieve with 0.25 mm holes. An option with a natural mixture of screening particles (NMP) is included in the experimental scheme. The particle size distribution of screenings is given in [11].

The content of CaCO₃ in dolomite is 46.1%; MgCO₃ is 38.4%.

In the experiment used *Umbric Albeluvisol Abruptic*: pH_{KCl} – 4.6; Ng – 4.9 mmol(eq)/100 g of soil, humus – 2.18. Particle content less than 0.01 mm – 21.4%.

In experiment No. 2, the composition of OMCs migrating from *Umbric Albeluvisol Abruptic*, reclaimed by CC (waste from the production of mineral fertilizers), was established in an amount of 2.5 Ng 20.25 t/ha. The chalk content of CaCO₃ is 90%. Soil samples were taken from the vessels of the growing experiment 5 years after reclamation. *Umbric Albeluvisol Abruptic* was used for the growing experiment: pH_{KCl} – 4.1; Ng – 5.4

mmol(eq)/100 g of soil; humus – 3.02%. Particle content < 0.01 mm was 18.6%. The experimental conditions are described in detail in [13].

The determination of carbon in the composition of the sediments was carried out according to the method of I.V. Tyurin, based on the oxidation of humus with a sulfur-chromium mixture in a ratio of 1:1. The optical density of OMC was measured at FEC, pre-dissolving the precipitate in 0.1 N NaOH. The method of T.A. Plotnikova, V.V. Ponomareva [14] was used. The wavelength was 430 nm, the thickness of the cell was 1 cm.

The content of Al, Mn, and Fe in the sediments was determined on an ICPE-9000 emission spectrophotometer (Shimadzu, Japan) according to the manufacturer's method. For this, the samples were ground and ashed in a mixture of concentrated HNO₃ and 38% H₂O₂ (1:1) at 70 °C using the DigiBlock system (LabTech, Italy).

3 Results and discussion

The maximum reclamation effect of liming (table 1) was achieved in the experimental variants using DF, a natural mixture of dolomite fractions (NMP) and particles of 7-10 mm in size (pH_{KCl} was established at the level of 5.6-5.7 units). The effect of using particles with a size of 5-7 mm was lower (pH_{KCl} 5.3). In experiment No. 2, 5 years after liming and placement in columns, pH_{KCl} of the soil is close to neutral (pH_{KCl} 6.3).

Table 1. Composition of organo-mineral complexes washed out from reclaimed *Umbric Albeluvisol Abruptic*.

Experiment option	pH _{KCl}	C _{total} , %	E _s mg/ml	Metal content, mg/kg			
				Al	Fe	Mn	Total
Experience No. 1 (ameliorant - dolomite crumb)							
1. NPK (background) + Dolomite (D) < 0.25 mm (1 Ng)	5.7 ± 0.1 b	5.60 ± 0.04 b	3.1 ± 0.3 a	1333 ± 39 b	167 ± 3 a	2640 ± 4 b	4139 ± 43 b
2. Background + D 5-7 mm (1 Ng)	5.3 ± 0.1 a	5.69 ± 0.01 c	2.7 ± 0.1 a	3968 ± 14 e	496 ± 3 d	18716 ± 95 e	2318 ± 91 a
3. Background + D 7-10 mm (1 Ng)	5.6 ± 0.1 b	5.59 ± 0.01 b	2.9 ± 0.1 a	3253 ± 13 d	424 ± 4 c	13635 ± 23 d	17372 ± 28 d
4. Background + NMP (1 Ng)	5.7 ± 0.1 b	5.51 ± 0.01 a	2.8 ± 0.1 a	1861 ± 4 c	359 ± 6 b	4356 ± 10 c	6576 ± 6 c
Experience No. 2 (ameliorant - conversion chalk)							
1. NPK (background) + CC (2.5 Ng)	6.3 ± 0.1 c	5.50 ± 0.02 a	3.0 ± 0.3 a	1693 ± 11 a	605 ± e	903 ± 7 a	3202 ± 29
Mean values and (±) standard errors of the mean (n = 3) are indicated. Different Latin letters indicate significant differences between the options according to the criterion of the smallest average difference (SAD) of Fisher (P <0.01).							

The amount of Corg in OMC ranged from 5.5 to 5.7%.

The optical density Esmg/ml of OMC in experiment No. 1 ranged from 2.7 to 3.1 units. In experiment No. 2 – Esmg/ml = 3. This corresponds to the optical density of the FC, which fits into the range from 1 to 4 units [15].

The scale of Al migration in experiment No. 1 depended on the size of the particles. By the amount of aluminum removed during OMC migration, all the studied variants can be arranged in the following descending sequence: particles with sizes 5-7 mm> 7-10 mm> NMP > particles less than 0.25 mm. The use of finely divided dolomite (<0.25 mm) reduced the migration mobility of aluminum by 2.98 and 2.44 times, respectively. The

amount of migrating aluminum in the OMC composition of experiment No. 2 with CC was higher than in the variant with DF and lower than in the variant with NMP in experiment No. 1.

In experiment No. 1, the content of manganese migrating as part of OMC ranged from 2639.5 to 18715.6 mg/kg. This was 1.98-4.71 times the amount of aluminum. The amount of migrating manganese in experiment No. 2 was 1.88 times less than that of aluminum.

The influence of the degree of grinding of dolomite on the amount of manganese bound in the composition of OMC is much stronger than that of aluminum.

Depending on the experiment option, the content of migrating iron was 7.7-8.0 times less than aluminum and 15.8-32.1 times lower than manganese. In experiment No. 1, the amount of washed iron ranged from 166.8 mg/kg (option with DF) to 495.9 mg/kg (option with particles 5-7 mm in size). The difference was 2.97 times.

In experiment No. 1, the migrating elements formed the following descending sequence: Mn > Al > Fe. In experiment No. 2, the content of washed Al in OMC exceeded the contents of Fe and Mn by 2.8 and 1.87 times, respectively.

Fulvic acids migrating as part of OMC bind a large amount of Ca, Mg, and Sr (Pavlova et al., 2018). The smaller the grinding fineness of dolomite, the more alkaline earth metals migrated as part of OMC. In experiment No. 1, fluctuations in their total content ranged from 191 to 319 g/kg of precipitate. Base-averaged FAs retain “aggressiveness” with respect to soil minerals, transferring Al, Mn, and Fe into a solution. The larger the particle size of the ameliorant and the smaller the bases Ca, Mg and Sr contain OMC, the higher the “aggressiveness” of FA. The relationship between the total amount of Ca, Mg, and Sr washed out and the sum of Al, Mn, and Fe migrating in experiment No. 1 is weak negative: $r = -0.2$. Using even 20.25 t/ha of CC does not eliminate the destruction of minerals.

Consequently, the processes of acid hydrolysis of minerals in reclaimed soils do not stop. Liming does not eliminate the influence of climatic factors on the processes of humus formation. The resulting humic acids remain acidic and even after neutralization with lime ameliorants, some functional groups have a destructive effect on soil minerals.

4 Conclusions

1. The content of carbon migrating as part of OMC in sod-podzolic reclaimed soils ranged from 5.5 to 5.7%. The OMC optical density values were within the range typical for fulvic acids ($E_s^{\text{mg/ml}} = 2.7\text{-}3.1$).
2. The processes of acid hydrolysis of minerals in lime soils do not stop. The total amount of Al, Mn, and Fe washed out in the OMC composition depended on the size of the ameliorant particles, the weathering of the surface of its particles, and the content of alkaline-earth metals in the OMC. Fluctuations in the total content of typomorphic elements in OMC in various experiment options with dolomite particles ranged from 2317.8 to 13371 mg/kg. In the experiment with CC, they were 3201.6 mg/kg.
3. Regardless of experiment option with dolomite particles, the migrating typomorphic elements formed the following descending sequence: Mn > Al > Fe. The content of eluted manganese was 7.7–8.0 times higher than the amount of aluminum washed out and 15.8–32.1 times the amount of migrating iron. In the experiment with CC, the content of washed aluminum in the OMC composition exceeded the content of Fe and Mn by 2.8-1.87 times, respectively.

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