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Dynamics of pH_{KCl} of reclaimed *Umbric Albeluvisol Abruptic* by ameliorants of various chemical nature

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Abstract

In the paper, changes of pH value during 20 days of soil interaction with the solution have been traced. Differences in the reaction rate using ameliorants of different chemical nature for liming have been established. It was revealed that the ameliorative effect of using materials of silicate nature in the experiment was lower than that of carbonate nature. According to the effect all ameliorants used in the experiment can be arranged in the following descending order: dolomite flour (DF), crushed stone sieve (CSS) > conversion chalk (CC), dolomitized limestone flour (DLF) > blast furnace slag (BFS) > oil shale ash (OSA). For all lime fertilizers empirical models of pH_{KCL} value change over the whole experimental interval were developed. Clustering of separate variants of the experiment, produced by different ameliorants on their influence on the index pH_{KCL} on the whole interval of study was carried out.

Keywords: reclamation, soil acidity, dolomite, limestone, blast furnace slag, oil shale ash.

Introduction

The laboratory of soil amelioration at the Agrophysical Research Institute of St. Petersburg has been conducting studies of the rate of ameliorants decomposition in soils for a long time (Litvinovich et al., 2001, 2016a, 2016b, 2021, 2022; Pavlova et al., 2020). It has been established that dissolution of calcareous materials in soils is prolonged in time and depends on their hardness, chemical composition, fineness of grinding, duration of interaction of ameliorant with soil, initial acidity of soils, uniformity of distribution of ameliorant in arable layer (Litvinovich et al., 2012).

It is known that when the soil containing residual amount of unreacted carbonates is exposed to 1n KCl solution, conditions for accelerated reaction lime-ameliorant are created (Nebolsin et al., 2005). Thus, Litvinovich et al. (2010) established the shift of pH_{KCL} of freshly limed soil with dolomite and limestone flour in 1n KCl salt suspension. It was shown that the soil-lime reaction did not terminate after one hour of shaking the suspension. During the 10-hour interaction, an increase in the pH values of the salt suspension was observed both in the

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variant with the use of limestone and dolomite flour. The obtained effect can be connected with accelerated decomposition of ameliorant particles by HCl, which is obtained by displacement of hydrogen ions from the soil absorbing complex by potassium cations. Exchange reactions of unreacted $CaCO_3$ and $MgCO_3$ with KCl could also take place, resulting in the formation of solutions of alkaline salts of potassium carbonates and bicarbonates (Nebolsin et al., 2005).

The present work is a continuation of the experiments started by Litvinovich et al. (2010). The aim of the research was 1) to study the dynamics of pH value in 1n KCl solution during 20 days of interaction of ameliorants of different chemical nature with acid sod-podzolic sandy loam soil fertilized with complex mineral fertilizer; 2) to develop empirical models of pH_{KCL} change depending on the time of fresh limed soil in salt suspension.

Material and methods

The calculated amount of complex mineral fertilizers and finely ground ameliorants was added to the dried and passed through a sieve with the diameter of holes 1 mm. The soil was poured with 1n KCl solution in 2.5 ratio. The suspension was shaken for 3 minutes and left for 24 hours. Then, the value of pH_{KCL} was determined in the suspension on an ionometer "Anion 7000". After measurement of pH_{KCL}, the suspension was shaken again and left for 24 hours. The change of pH_{KCL} of the suspension was carried out daily for 20 days.

A very strongly acidic sod-podzolic sandy loam soil (*Umbric Albeluvisol Abruptic*) from a natural perennial meadow was selected for the experiment. Gross chemical and granulometric compositions of soils are given in Tables 1 and 2.

Table 1. Granulometric composition of sandy loamy sod-podzolic soil

Fraction size, mm	1-0.25	0.25-0.05	0.05-0.01	0.01-0.005	0.005-0.001	< 0.001	<0.01
Content, %	1.77	58.14	21.50	5.95	7.04	6.86	18.6

Table 2. Gross chemical composition of soil, %

Loss on ignition	SiO_2	R_2O_3	Fe_2O_3	Al_2O_3	CaO	MgO	P_2O_5	SO_3
6.15	81.09	9.28	1.19	7.97	0.44	0.47	0.11	0.51

Physico-chemical characteristics of soil are as follows: pH_{KCL} 3,76; Hy - 11,75 mmol(eq)/100 g; humus - 3 %; content of particles < 0,01 mm - 18,6 %. The content of mobile calcium is 1366 mg/kg. Six types of ameliorants of carbonate and silicate nature were used for research. Chemical composition of ameliorants is presented in Table 3.

Table 3. Chemical composition of ameliorants

Ameliorant	Mass fraction of CaO, %	Mass fraction of MgO, %	Mass fraction of SiO2, %
Conversion chalk (CC)	50.7	1.7	–
Dolomitized limestone flour (DLF)	44.7	4.3	–
Dolomite flour (DF)	30.4	21.0	–
Blast furnace slag (BFS)	39.7	19.7	38.5
Oil shale ash (OSA)	42.1	4.2	27.1
Crushed stone screening (CSS)	27.0	17.3	–

Conversion chalk (CC) is a synthetic calcium carbonate obtained as a waste product from nitrogen fertilizer production as a result of nitric acid decomposition of apatite concentrate. It has a finely dispersed granulometric composition (Kabanina et al., 1984). Its detailed ameliorative properties are given in Lavrishchev (2000) and Lavrishchev et al., (2019).

Dolomite flour (DF) and Dolomitized limestone flour (DLF) are produced from the dolomite rock in Vitebsk, Republic of Belarus. It contains calcium and magnesium carbonate salts ($CaCO_3$ + $MgCO_3$).

Blast furnace slag (BFS) is a waste product of ferrous metal production. Blast furnace slag from Severstal Cherepovets steel plant (Russia) was used in the experiment as a lime-silicate fertilizer. Comparative analysis of fertilizing value and ameliorative properties of DF and BFS is given in (Litvinovich et al., 2013, 2023).

Oil shale ash (OSA) is formed by burning oil shale at large power plants and small boiler houses equipped for their combustion in a "fluidized" bed at a temperature of about 1000 °C. In our research we used ash from the Kohtla-Järve, Estonia. Silicates and calcium oxides are present in the composition of the active substance of the ash. The presence of magnesium was also found.

Crushed stone screening (CSS) is a waste from carbonate rocks (dolomite screening), intended for road construction from the Elizavetino deposit (Gatchina district, Leningrad region, Russia). Fractions smaller than 10 mm are sifted into dumps. Fertilizing value and ameliorative properties of the waste are presented in Litvinovich (2016a).

Before application to the soil, all ameliorants were crushed and passed through a sieve with a hole diameter of 0.25 mm. Doses of ameliorants were equalized by neutralizing ability. The scheme of the experiment is given in Table 4. All variants of the experiment were carried out in 4 replications.

For the comparison variants without application of any chemicals (treatment No 1), as well as soil fertilized with NPK 16:16:16 and APAVIVA (variants 2, 3) by 0.2 g per 1 kg of soil weight were studied. In the ameliorated variants, APAVIVA was applied as a background fertilizer.

APAVIVA - (NPK 15:15:15:15) is produced by PJSC "PhosAgro" (Russia). Nitrogen in the fertilizer is presented in the form of NH^{4+}, 90% of phosphates are water-soluble forms. It contains 10% sulphur and 0.3-1% MgO.

The necessary amount of ameliorant for liming was established from the calculation of hydrolytic acidity elimination by 1Hy. Recalculation was carried out on the mass of arable layer 3000 tons. The empirical models were built according to Bure (2007).

Results and Discussions

Variation of pH_{KCL} value in the variants of the experiment is shown in Table 4. The data of the table show that the pH_{KCL} value of the suspension in the control variant of the experiment fluctuated from 3.64 to 3.85 units, i.e. remained in the range of very strongly acidic.

Comparative analysis of the pH_{KCL} dynamics data in the variants using APAVIVA and azofoska did not reveal significant differences between them. The pH_{KCL} fluctuations over the entire study interval amounted to: azofoska - 3.56-3.86, APAVIVA - 3.59-3.83 pH units. As in the control variant of the experiment, the value of pH_{KCL} was within the interval of strongly acidic. Neither acidification nor alkalinization of the soil did not occur with the use of complex fertilizers.

A different picture was established when analyzing the data of pH_{KCL} change in freshly limed soils. In the variant with application of conversion chalk a day after infusion the value of pH_{KCL} amounted to 4.8 units (average acidic interval of values) and remained at the same level till the end of the experiment. On the average, during the whole observation period, there were no significant changes in the pH value. Model (1) of the dynamics of the pH_{KCl} value change is not statistically significant (Table 5). The model graph is shown in Fig. 1.

Table 4. Dynamics of pH KCl, freshly limed soil with ameliorants of different chemical composition

Treatment	Day										
	0	1	2	3	4	5	6	7	8	9	10
1. Control (without fertilizer)	3.76	3.64	3.69	3.69	3.72	3.74	3.72	3.77	3.81	3.83	3.85
2. Azofoska	3.76	3.56	3.63	3.65	3.69	3.73	3.71	3.75	3.82	3.82	3.86
3. APAVIVA	3.76	3.59	3.66	3.67	3.71	3.75	3.73	3.77	3.81	3.83	3.87
4. APAVIVA + CC at 1Hy	3.76	4.80	4.88	4.86	4.93	4.99	4.94	4.93	4.98	4.97	5.00
5. APAVIVA + DLF at 1Hy	3.76	4.97	4.83	4.85	4.91	4.90	4.98	4.94	4.94	4.99	4.99
6. APAVIVA + DF at 1Hy	3.76	4.53	4.71	4.80	4.93	4.99	5.06	5.07	5.15	5.15	5.20
7. APAVIVA + CSS at 1Hy	3.76	4.63	4.85	4.96	5.08	5.12	5.17	5.16	5.23	5.20	5.23
8. APAVIVA + OSA at 1Hy	3.76	3.74	3.82	3.86	3.89	3.92	3.92	3.97	4.04	4.04	4.09
9. APAVIVA + BFS at 1Hy	3.76	4.05	4.21	4.28	4.37	4.45	4.46	4.50	4.60	4.62	4.66
	Day										
	11	12	13	14	15	16	17	18	19	20	
1. Control (without fertilizer)	3.82	3.83	3.72	3.78	3.77	3.74	3.81	3.79	3.79	3.80	
2. Azofoska	3.79	3.81	3.72	3.79	3.77	3.73	3.75	3.74	3.74	3.76	
3. APAVIVA	3.81	3.85	3.72	3.80	3.78	3.75	3.77	3.80	3.77	3.78	
4. APAVIVA + CC at 1Hy	4.93	4.93	4.88	4.92	4.89	4.88	4.87	4.72	4.69	4.84	
5. APAVIVA + DLF at 1Hy	4.93	4.93	4.89	4.93	4.90	4.86	4.89	4.80	4.65	4.82	
6. APAVIVA + DF at 1Hy	5.14	5.15	5.10	5.18	5.14	5.11	5.15	5.03	4.91	5.04	
7. APAVIVA + CSS at 1Hy	5.18	5.17	5.14	5.19	5.16	5.13	5.15	5.02	4.95	5.03	
8. APAVIVA + OSA at 1Hy	4.04	4.07	3.97	3.98	3.99	3.95	3.97	3.97	3.67	3.84	
9. APAVIVA + BFS at 1Hy	4.63	4.64	4.58	4.65	4.65	4.61	4.65	4.60	4.44	4.51	

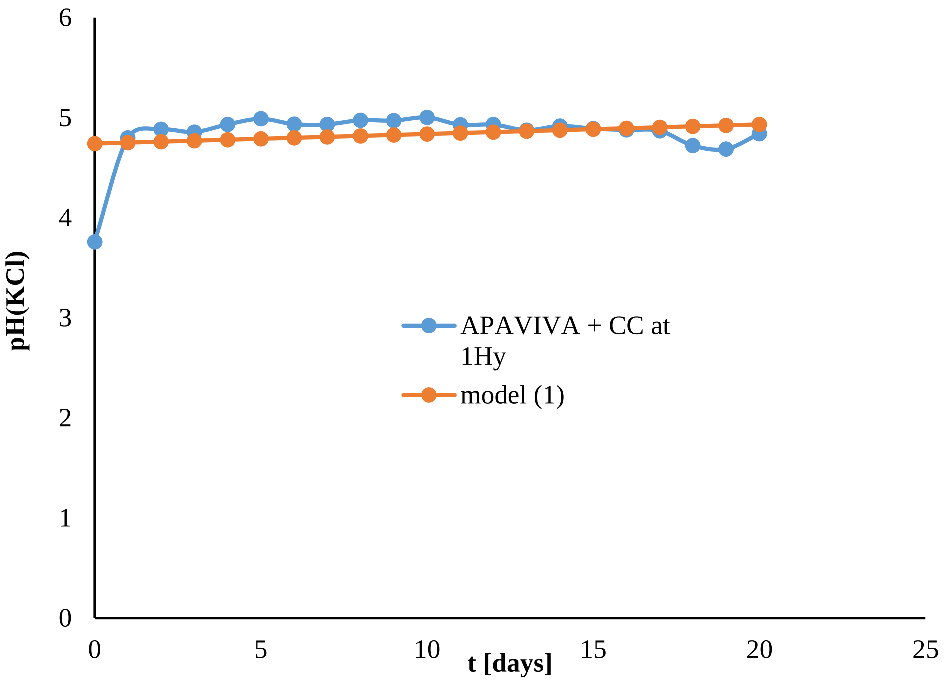

Fig. 1. Dynamics of pH_{KCL} value in soil ameliorated by CC

The character of pH value change when using dolomite and dolomitized limestone flour (DLF) differed from each other. In the variant with DLF, the maximum pH shift was reached a day after suspension infusion (4.97 pH units). Further, during the whole period of study, the fluctuations were not significant and fell within the range corresponding to the average acidic pH values.

Table 5. Empirical models which describe the changes of pH_{KCL} in salt suspension depending on the time of interaction between soil and ameliorant

No.	Ameliorant	Model	p-value	R^2
1	CC	$y_1 = 4{,}74 + 0{,}0096 \cdot t$	0.3	0.05
2	DLF	$y_2 = 4{,}75 + 0{,}0092 \cdot t$	0.34	0.048
3	DF	$y_3 = 4{,}66 + 0{,}03 \cdot t$	0.005	0.34
4	CSS	$y_4 = 4{,}78 + 0{,}024 \cdot t$	0.034	0.215
5	OSA	$y_7 = 3{,}89 + 0{,}004 \cdot t$	0.31	0.052
6	BFS	$y_8 = 4{,}21 + 0{,}026 \cdot t$	0.0003	0.499

In the treatment with DF application the effect after a day of infusion was lower (4.53 pH units). The growth of pH values continued until the middle of the experiment (10 days after liming) - 5.2 pH units. Then, there was a tendency of gradual decrease of pH value.

The similar character of dynamics of pH value change in soil suspension was established in the variant with the use of finely ground dolomite sift for liming. Models Nos. 2, 3 and 4 of pH value change when using for liming ameliorants of carbonate nature are statistically insignificant during the whole period of study (Table 5). Graphs of models are shown in Figs. 2, 3 and 4.

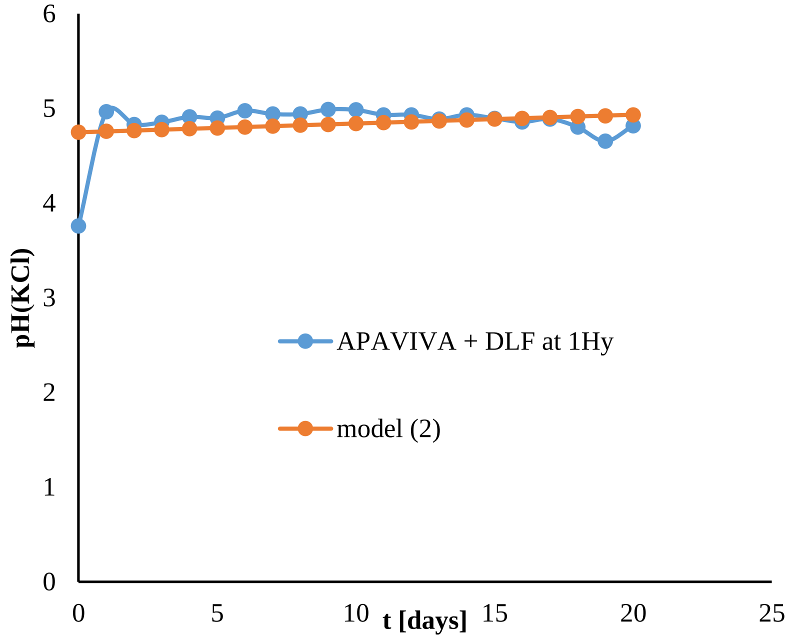

Fig. 2. Dynamics of pH_{KCL} value in soil ameliorated by DLF

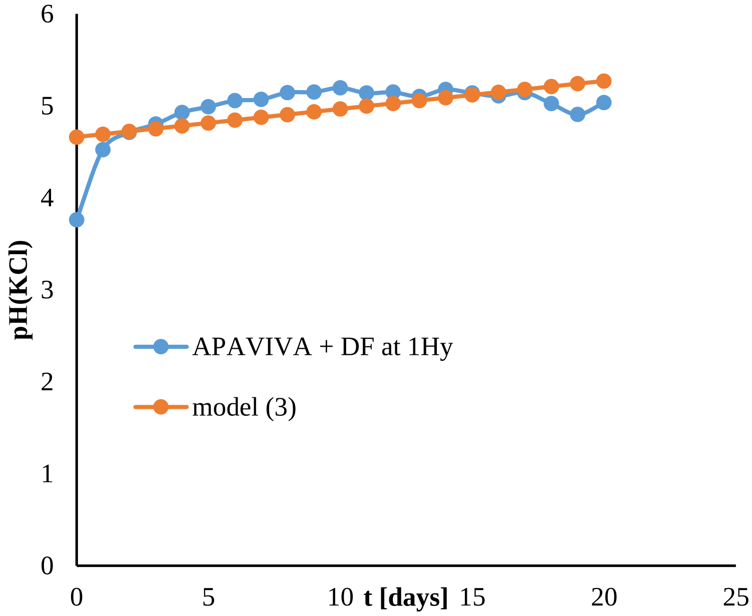

Fig. 3. Dynamics of pH_{KCL} value in soil ameliorated by DF

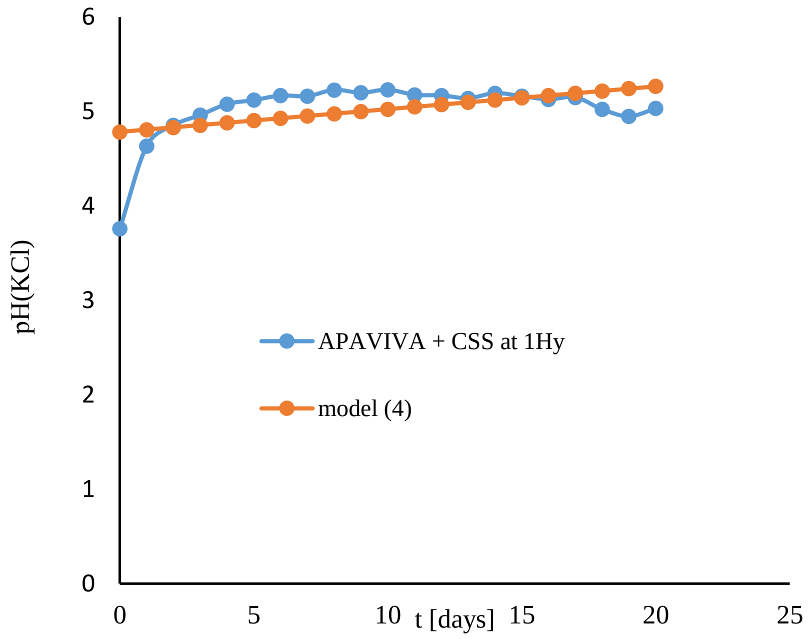

Fig. 4. Dynamics of pH_{KCL} value in the soil ameliorated by CSS

Ameliorants of silicate nature in the experiment are represented by industrial wastes: blast furnace slag and shale ash. The effect from application of these ameliorants was lower than ameliorants of carbonate nature. Fluctuations of pH value did not go beyond average acidic values. Thus, the growth of pH value in the variant with DS was observed up to the 8th day of study (4.60 pH units). Up to 18 days of ameliorant interaction with soil, pH value remained practically unchanged (4.6-4.66 pH units). Then there was a tendency to decrease of pH value of salt suspension.

The least ameliorative effect was characterized by shale ash. Maximum shift of pH values in some periods of observations did not exceed 0.3-0.4 pH units. Models Nos. 7 and 8 describing the dynamics of pH value change in the soil of variants ameliorated by OSA and BFS are statistically significant (Table 5). Graphs of the models are shown in Figs. 5 и 6.

Thus, the ameliorative effect of the materials of silicate nature in the experiment was lower than that of carbonate nature. According to the effect achieved as a result of liming, all ameliorants used in the experiment can be arranged in the following descending order: dolomite flour, crushed stone screening > conversion chalk, dolomitized limestone flour > blast furnace slag > shale ash.

Analysis of models of KCl value change in variants with different ameliorants allowed to establish the following:

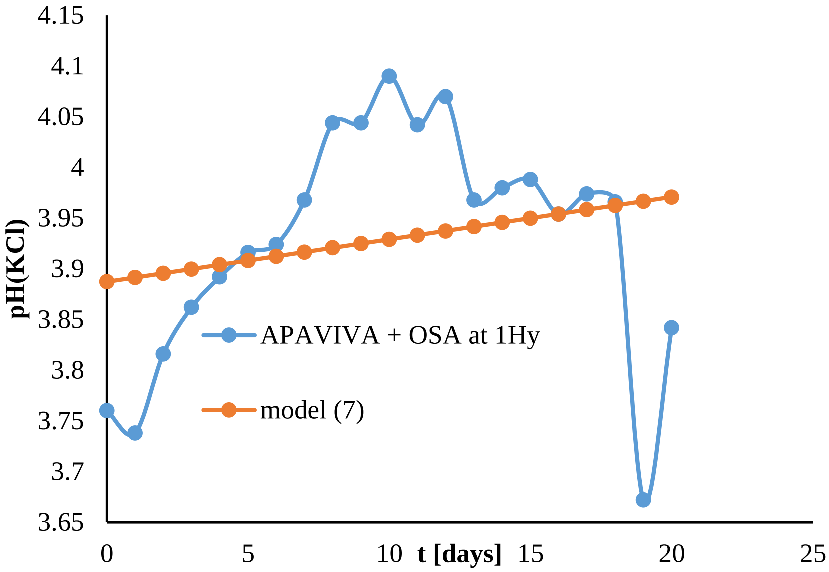

Fig. 5. Dynamics of pH_{KCL} value in soil ameliorated by OSA

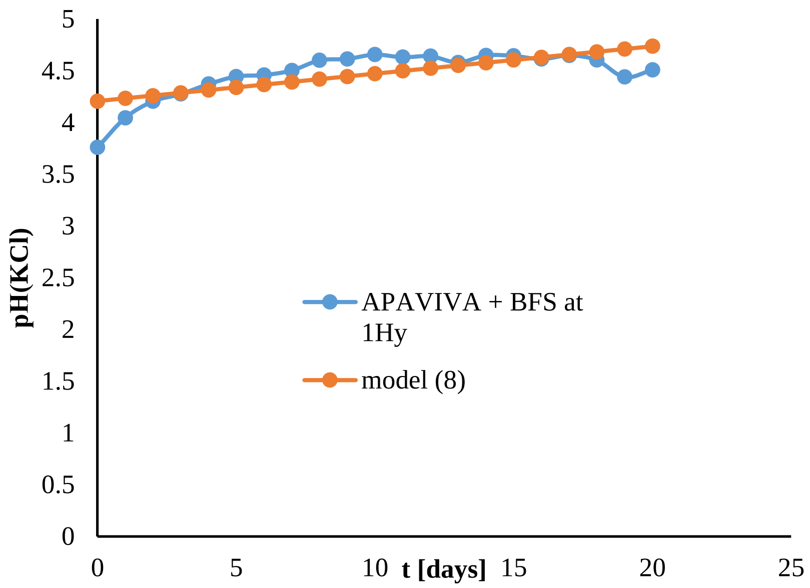

Fig. 6. Dynamics of pH_{KCL} value in soil ameliorated by BFS

Empirical model (3) in variant 6 is statistically significant at high level of values. In this variant of the experiment there is a statistically significant change in pH in average (pH increases).

Empirical models (4, 6) - have high statistical significance, there is an increase in pH.

Empirical models (1), (2), (5) are statistically insignificant, there is no significant change in pH on average over the entire study interval.

The empirical models (1) and (2) are very similar, the coefficients of the models are close in their values. As can be seen from the graphs, the dynamics in the variants of experiment 4, 5 are very similar (no statistically significant changes in pH on average over the entire interval of observation).

Despite the lack of statistical significance, the empirical model (5) differs markedly from models (1), (2) by the values of coefficients and, as can be seen from the graph, the nature of dynamics in the variant of experiment 7 differs markedly from the variants of experiments 4, 5.

There is an undoubted similarity of models (4) and (6), the coefficients of the models are close in their values and, as can be seen from the graphs, the dynamics of pH_{KCL} change is very similar (statistically significant changes occur).

In general, the following groups of experiments can be distinguished on the basis of the conducted research:

Group I includes variant	6 (background + dolomite flour at 1 Hy)
Group II includes variants	7 (background + crushed stone sift at 1 Hy)
	9 (background + blast furnace slag at 1 Hy).
Group III includes variants	4 (background + con. chalk at 1 Hy)
	5 (background + dol. flour at 1 Hy).
Group IV includes variant	8 (background + shale ash at 1 Hy).

Conclusion

When ameliorants of different chemical nature are applied to sod-podzolic sandy loam soil, conditions for acceleration of soil:ameliorant reaction in 1n KCl solution are created. The reaction in suspension does not end after 1 day of ameliorant interaction with soil.

According to the effect all ameliorants used in the experiment can be arranged in the following descending order: dolomite flour, crushed stone sift > conversion chalk, dolomitized limestone flour > blast furnace slag > shale ash. When using lime materials of silicate nature, the ameliorative effect was lower than that of ameliorants of carbonate nature.

Empirical models describing changes of pH_{KCL} value for 20 days of "soil- ameliorant" reaction both for ameliorants of carbonate and silicate nature were developed. The clustering of separate variants of the experiment, produced by different ameliorants on their influence on the pH_{KCL} value during the whole period of study was carried out.

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Динамика pH_{KCl} у *Umbric Albeluvisol Abruptic* мелиорансима различите хемијске природе

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Izvod

У раду је приказана могућност убрзане реакције мелиорантно-свеже кречованог земљишта у 1н раствору калијум хлорида. Праћене су промене pH вредности током 20 дана интеракције земљишта са раствором. Утврђене су разлике у брзини реакције коришћењем мелиоранса различите хемијске природе. Утврђено је да је мелиоративни ефекат употребе материјала силикатне природе у експерименту мањи од карбонатног. Према постигнутом ефекту кречњавањем, сви мелиоранти коришћени у огледу могу се распоредити у следећем опадајућем реду: доломитно брашно (DF), крхотине од ломљеног камена (CSS) > конверзиона креда (CC), доломитизовано кречњачко брашно (DLF).) > шљака високе пећи (BFS) > пепео из уљних шкриљаца (OSA). За сва кречна ђубрива развијени су емпиријски модели промене pH_{KCL} вредности током целог експерименталног интервала. Извршено је груписање одвојених варијанти експеримента, произведених од различитих мелиоранти на њихов утицај на индекс pH_{KCL} у целом интервалу истраживања.

Кључне речи: мелиорација, киселост земљишта, доломит, кречњак, шљака високе пећи, пепео из уљних шкриљаца

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