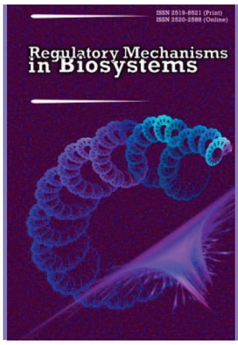

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Use of model representations of convectional diffusion for determination of indicators of phosphate sorption and solubility in chernozem soils

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The problem of effective use of phosphate fertilizers is largely determined by the dynamics of transformation of the residue of orthophosphoric acid $H_2PO_4^-$ into readily available compounds of calcium monophosphate and calcium diphosphate, with their subsequent transition into poorly soluble forms of calcium phosphates. These processes were studied in the static equilibrium systems, whereas the real processes of migration and transformation of phosphorus compounds in the soil profile are always associated with the dynamics of vertical convective motion. The paper proposes the eluate wave method based on the developed methodology with the use of convectional diffusion concepts to perform a quantitative assessment of the main characteristics of complex adsorption and transformation of the residue of orthophosphoric acid $H_2PO_4^-$ in the diffusion process in ordinary and southern light/medium loamy chernozems with a certain level of salinity. During the experiment, the process of frontal filtration of easily soluble phosphates was simulated in a column filled with soil under the action of a convection flow of water. At the exit of the column, partial volumes of filtrate normalized according to the fixed time interval of 30 minutes were taken. Because of the different filtration rates determined by the type of soil under study, partial volumes were different and varied from 200 to 300 mL. Quantitative assessment of phosphates in the partial volumes allowed us to establish the Gaussian-type time dependence with a clearly expressed asymmetry of ascending and descending parts of the eluate wave as a consequence of changes in sorption and diffusion characteristics, i.e. mobility of phosphates as they move in the filtration column. Depending on the structure of the mechanical composition and salinity of soils, the diffusion coefficient reflecting the phosphates' mobility in the soil profile on the concentration gradient varied from 0.15 to 0.57 cm^2/min. With the increase in the absorbed base amount from 23.5 to 34.2 mmol/100 g, the sorption coefficient rose from 3.6 to 6.5, that is, even in the presence of the average level of salinity, the amount of strongly bound phosphates almost doubled. Experimental values of the total volumes of filtrate varied from 7.99 to 15.65 L depending on the type of soil (with the initial introduction into the upper part of the column of the $H_2PO_4^-$ amount corresponding to 9.92 g of the composition $Ca(H_2PO_4)_2/CaHPO_4$ in the ratio of 60% and 40%). Our findings were used as a basis for calculation of the rates of application of phosphate fertilizers, taking into account the actual moisture content in the soil, in order to ensure their maximum possible solubility and efficiency of use by agricultural plants.

Keywords: mobility of phosphates; soil; sorption coefficient; filtration; eluate wave.

Introduction

One of the problems of modern agricultural technologies is the effective use of phosphate fertilizers, since a significant part of the applied fertilizers, about 40%, is actually not used by the plants due to low solubility of phosphates in the soil solution or their fixation in the soil absorption complex (Chien, 1993; Ghosal & Chakraborty, 2012; Meyer et al., 2018). Phosphorus-buffering capacity of soils is largely determined by the ability of the solid part of the soil to immobilize and adsorb mineral phosphorus compounds. The reverse process of mobilization and desorption of these compounds into the soil solution ensures their availability to plants (Zubkovska, 2024). Soils have the ability to absorb both cations and anions. This process may occur in the form of ion exchange, but chemical absorption and chemisorption are observed for the phosphates as well.

Using the concept of convective diffusion (Filipović et al., 2020) can describe not only the physical sorption, but also the transition of a substance from solution to sediment due to formation of poorly soluble compounds. If the phosphate adsorption is understood as the transition of phosphates from solution to solid phase of the soil, this process is theoretically described by the Freundlich and Langmuir adsorption equations (Kruse et al., 2015), regardless of the reaction mechanism: physical sorption, chemisorption, or precipitation. Since soils contain a sufficiently large sum of absorbed bases, primarily Ca, Mg and Na, which is particularly undesirable in terms of salinity, phosphorus becomes fixed in the soil solution because of the formation of strong bonds with the mineral components in the soil (Zhang et al., 2014; Argotte-Ibarra et al., 2022).

The major part of natural phosphates is represented by orthophosphates, mainly calcium ones, comprising about 80–90% (Nosko, 2017). Calcium carbonates and bicarbonates have a significant sorption capacity in relation to phosphates. A high content of the above substances is typical for the ordinary chernozems and southern chernozems, as well as for podzolic soils (Nosko, 2018; Kedir et al., 2022). Initially the amorphous calcium phosphates are formed on the surface of carbonates during chemisorption, and further they turn into practically insoluble crystalline forms. At the low concentration of phosphorus in the solution, mainly hydroxylapatite is formed on the surface of calcium carbonates, while octacalcium phosphate is formed at the high concentration. The application of phosphate fertilizers to soil with high sorption capacity can be inefficient, as phosphorus is largely accumulated in the soil in the hardly soluble forms. The bioavailability of soil phosphorus is determined by exchange processes in the solid phase – soil solution system. The rate of exchange between phosphate ions in solution and inorganic phosphate in the soil can be estimated by the parameters of isotope exchange kinetics (Helfenstein et al., 2018).

As is commonly known (Eduah et al., 2020; Teles et al., 2020; Rupngam et al., 2023), the ability of a chemical compound to dissolve is expressed by the product of the molar concentrations of ions of this compound in the saturated solution, which reflects an indicator of the solubility product. The negative logarithm of this pK value quantitatively characterizes the solubility of this compound. The higher the pK value, the lower the compound solubility. For example, for rather poorly soluble dicalcium phosphate compound (0.2 g/L), the logarithm of the solubility product is $pK = pCa + pHPO_4 = 6.66$, while the corresponding values for hydroxylapatite are $pK = 10pCa + 6pPO_4 + 2pOH = 113.7$, and for octacalcium phosphate $pK = 4pCa + pH_3 + pPO_4 =146.9$ (Wild, 1964). These compounds have very low solubility and are actually withdrawn from the phosphorus metabolism of the soil.

Therefore, the problem of effective use of phosphate fertilizers is largely determined by the dynamics of transformation of the residue of orthophosphoric acid $H_2PO_4^-$ into easily soluble compounds of calcium monophosphate $Ca(H_2PO_4)_2$ and calcium diphosphate $CaHPO_4$ and their subsequent transition into poorly soluble forms of calcium phosphates (Messiga et al., 2021).

The sorption capacity of soil and its filtration characteristics with regard to active forms of phosphorus are characterized by the distribution and diffusion coefficients (Makowski et al., 2020). The distribution coefficient is the ratio of the amount of substance adsorbed per unit mass of the soil to its concentration in the equilibrium solution. The diffusion coefficient characterizes the rate of diffusion of phosphorus compounds in relation to their concentration gradient. These two indicators are used in this paper for the development of a simulation model to predict filtration and redistribution of phosphorus compounds in the soil horizon.

There are several methods for the determination of adsorbed ions and coefficients of their distribution in the soil structures (Buehler et al., 2002; Kruse et al., 2015; Kadyampakeni et al., 2017), each method has certain limitations in its application and interpretation of results. The method for studying the distribution in the equilibrium solution, according to which the weight fraction of the solution as a rule significantly exceeds the weight fraction of the solid phase (1:50), gives incorrect results since in real conditions, even with total moisture capacity of the soil, the weight fraction of water does not exceed 40%. The method of centrifugation is more acceptable as it allows one to obtain relatively correct estimates of the distribution coefficients. However, it also has some deficiencies, since the values of the distribution coefficient depend significantly on the centrifugation speed, due to the presence of a water layer adsorbed on the surface of soil particles, where the content of soluble forms and other ions differs from the content in the gravitation water. The method of displacement has similar deficiencies and is quite difficult to implement.

The most acceptable method, which properly simulates the process of filtration and distribution of compounds in the soil, is the method of eluate wave, or frontal filtration in a column (Syrovatko, 2007; Raniro et al., 2022) filled with soil of total moisture capacity and density of 1.2–1.4 g/cm^3. Generally, it corresponds to the light and medium loamy soils considered in this paper. This method allows one to evaluate, in addition to the distribution coefficient, the rate of diffusion of ions, that is, the diffusion coefficient. The method of eluate wave is widely used in the quantitative chromatographic analysis, including organophosphorus compounds, while for the study of sorption and mobility of the phosphorus mineral compounds in specific soil structures it has not been used before.

The purpose of this paper is to develop a methodological approach for studying the dynamics of processes of sorption, solubility and mobility of phosphates in the soil based on the concepts of convectional diffusion and, accordingly, to conduct an experimental study of quantitative characteristics of phosphate behavior in soil varieties with the different mechanical composition and salinity.

Materials and methods

For studying the adsorption characteristics and mobility of phosphates, we used the soils of ordinary chernozems and southern chernozems (Table 1), which belong to various agro-productive groups (List of agro-productive soil groups, 2012. Resolution of the Academic Council of Ukraine No. 1051 of 17.10.2012 "On Approval of the Procedure for Maintaining the State Land Cadastre"). Varieties selected for each type of soil differ in their mechanical composition and agrochemical parameters (Tables 2, 3). Southern chernozem soil varieties are distinguished by increased content of dry residue, Na^+, K^+, Cl^- and HCO_3^- ions (Table 4), which characterizes them as soils undergoing salinization processes.

Table 1
Name of soils under study

Variant of experiment	Agro-productive soil group	
	code	name
1	61g	ordinary low-humus shallow chernozems and their residually and slightly-alkalinized light loamy varieties
2	61d	ordinary low-humus shallow chernozems and their residually and slightly-alkalinized medium loamy varieties
3	72g	southern chernozems and their residually and slightly alkalinized varieties along with steppe alkali soils (10–30%) light loamy varieties
4	72d	southern chernozems and their residually and slightly-alkalinized varieties along with steppe alkali soils (10–30%) medium loamy varieties

Table 2
Mechanical composition of soils under study (% content of fractions)

Code of agro-group	Particle size of fractions, mm						Sum of particles < 0.01
	sand		dust			silt	
	> 0.25	0.25–0.05	0.05–0.01	0.01–0.005	0.005–0.001	< 0.001	
61g	29.85	26.06	14.87	12.97	9.57	6.69	29.22
61d	27.90	18.76	16.85	15,13	12.75	8.61	36.49
72g	29.85	26.06	14.87	12.97	9.57	6.69	29.22
72d	28.58	18.97	14.97	15.58	12.92	8.98	37.48

Table 3
Agrochemical indicators of soils under study

Code of agro-group	Absorbing capacity, mmol/100 g	Ca^{2+}, mmol/100 g	Mg^{2+}, mmol/100 g	Na^+, mmol/100 g	Hydrolytic acidity, mmol/100 g	pH of water	Organic matter, %	$N\text{-}NO_3$, mg/kg	P_2O_5, mg/kg	K_2O, mg/kg
61g	23.48	16.08	6.99	0.41	0.67	7.4	3.67	3.67	134	145
61d	29.44	24.08	4.95	0.36	0.78	7.3	3.88	3.88	146	167
72g	32.48	26,12	5.99	1.41	0.27	7.9	3.67	3.67	134	175
72d	34.22	27.69	5.14	1.39	0.29	7.9	3.88	3.88	133	177

Table 4
Content of soluble salts in aqueous extracts of soils under study (mmol-eq.)

Code of agro-group	Dry residue, %	HCO_3^-	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+
61g	0.092	1.13	0.17	0.12	0.32	0.23	0.13	0.01
61d	0.133	1.53	0.21	0.15	0.65	0.54	0.19	0.03
72 g	0.820	9.99	1.00	0.12	0.29	0.24	3.98	1.78
72d	0.922	9.85	0.99	1.65	2.30	0.29	3.91	1.72

The eluate wave was formed in the glass column of L – 15 cm, R – 3.5 cm. The column was filled with the soil under study, which was previously crushed. The bottom of the column was made of the water- permeable material, securing free filtration of water over the column area into the changeable cuvettes. Before filtration, the soil placed into the column was moistened and brought to a state of total moisture capacity.

The limit content of phosphorus was formed on the filtration column surface by adding phosphates easily soluble in water. For this purpose, several layers of filter paper R 3.5 were used (white strip). The surface of the paper was uniformly impregnated with 85% orthophosphoric acid of density 1.88 g/mL in 5 mL volume, which contained 2.557 mg of P, or 7.908 g of $H_2PO_4^-$. The presence of this anion in the soil, according to the accepted terminology, is identified with the phosphate potential of the soil in molar terms.

For the formation of forced filtration, an additional column of L – 90 cm of the equal cross-sectional area was installed above the filtration column, with the constant water level of 90 cm high. Before filling with water, it was combined with the filtration column through a rubber adapter to eliminate any possible leakage.

Since the rate of volume filtration and, accordingly, linear filtration for the soils under study was different, a 30 minute time interval was taken as a discrete unit of measure for sequential selection of the portions of filtrate. Consecutively selected partial volumes of filtrate were analyzed for the phosphorus content by the photometric method using the complex of phosphomolybdic acid and stannic chloride as a reducing agent (DSTU 4115:2002. Soils). Determination of mobile phosphorus and potassium compounds by the modified Chirikov method. Kyiv: State Standard of Ukraine). The values obtained for the content of P_2O_5 were converted to phosphorus (P) content.

Next, using the graphic constructions based on the data of the temporal dynamics of changes in phosphorus content in the partial volumes of filtrates, we calculated the main parameters of phosphate mobility in the soil varieties under study according to the developed methodology, as described below.

The planning of the experiment and the analysis of its results are based on the modeling of the processes of transformation in time of absorbed and soluble forms of phosphates and the dynamics of their downward movement (eluate wave) in the filtration column developed by the authors.

According to the general theory of the dynamics of sorption and chromatography (Syrovatko, 2007; Kruse et al, 2015), the distribution of ions in the process of movement in the filtration column is described by a system of balance equations:

$$\frac{\partial u(x,t)}{\partial t}+\frac{\partial N(x,t)}{\partial t}=D\frac{\partial^2 u(x,t)}{\partial x}+V\frac{\partial u(x,t)}{\partial x} \quad (1)$$

$$\frac{\partial N(x,t)}{\partial t}=\psi(u,N),$$

where u(x,t) – time-dependent linear concentration of the compound in gravitation water; N(x,t) – time-dependent linear concentration of the sorbed compound; V – linear speed of filtration, cm/min; D – diffusion coefficient (cm^2/min); ψ(u,N) – function describing the relationship between the adsorbed and mobile fractions of the phosphorus compound.

In the first approximation, this relationship can be written in the form of a linear isotherm corresponding to the Langmuir equation:

$$u(x,t)=hN(x,t), \quad (2)$$

where h – distribution coefficient, or sorption index in the methodical representation of the potential buffer capacity (Campos et al., 2016). It is a dimensionless value characterizing the sorption isotherm of phosphorus compounds, that is, distribution between dissolved and adsorbed forms of phosphorus.

Taking into account the linear isotherm, the system of equations can be reduced to one equation:

$$\frac{\partial u(x,t)}{\partial t}\left(1+\frac{1}{h}\right)+V\frac{\partial u(x,t)}{\partial x}=D\frac{\partial^2 u(x,t)}{\partial x^2}, \quad (3)$$

Considering the value $1+1/h=(h+1)/h$ as a multiplier, equation (3) turns into the following:

$$\frac{\partial u(x,t)}{\partial t}+V'\frac{\partial u(x,t)}{\partial x}=H\frac{\partial^2 u(x,t)}{\partial x^2}, \quad (4)$$

where $V'=\frac{hV}{1+h}$; $H=\frac{hD}{1+h}$.

The method of eluate wave suggests the creation of a thin layer of phosphates easily soluble in water in the upper part of the filtration column. In this case, we form the corresponding boundary and initial conditions: t = 0; $0 \le x \le x_0$; $u(x, 0) = u_0$; $N(x0,0) = N_0$; $x > x_0$; $h(x0,0) = 0$; $N(x,0) = 0$.

We assume that there is sufficient time for the passage of the eluate wave over the total length of the column, i.e. complete washing by the convection flow of water. Under action of the diffusion and convection processes, the initial narrow zone is washed away during the filtration process. Distribution of phosphorus in this wave is satisfactorily described by the solution of equation (4), which is expressed by the Gaussian-type equation:

$$\varphi(x,t)=\frac{u(x,t)}{u_0}=\frac{u_0}{\sqrt{4\pi Ht}}\exp\left[-(x-V't)^2/4Ht\right], \quad (5)$$

Among the various concentration points of the wave, there is one maximum point that moves at a constant speed:

$$V_{\max}=x_{\max}/t=hV/(1+h)=V', \quad (6)$$

This point represents the average value in the distribution (5) and can actually be obtained from the properties of the extremum of the function $\frac{\partial u(x,t)}{\partial x}=0$; $x = x_{max}$.

Therefore, after determination of the speed of movement of the distribution maximum in the filtration column, and knowing the linear speed of filtration, we can find the distribution coefficient h. All other concentration points of the wave move at a variable speed. The wave width is conventionally taken as the difference in the coordinates of two concentration points of the wave, for which u/umax = e^{-1}. Then the relationship below is true

$$u/u_{\max}=\exp\left[-\frac{(x-V't)^2}{4Ht}\right]/\exp\left[-\frac{(x_{\max}-V't)^2}{4Ht}\right]=e^{-1}, \quad (7)$$

Since $x_{\max}=V't$, the denominator in (7) is equal to 1, and then

$$(x-x_{\max})=\pm 2\sqrt{Ht}; x_1=x_{\max}+2\sqrt{Ht}; x_2=x_{\max}-2\sqrt{Ht} \quad (8)$$

Thus, in the process of filtration the wave is expanded in proportion to $\sqrt{t}$. The maximum concentration in the wave is:

$$u_{\max}=\frac{u_0}{\sqrt{4\pi Ht}}, \quad (9)$$

that is, it decreases in inverse proportion to $\sqrt{t}$.

After a certain time t = t_1 the leading edge of the eluate wave reaches the lower edge of the column and can be recorded by direct measurement in the partial sample of a fixed volume, corresponding to the discrete sampling time. In the same way, we recorded the discrete time t_2 of the appearance of the last portion of filtrate of the end part of the wave. Knowing the values of V' and V – filtration rates according to (4), we calculated the main parameter h. Next, from the relationship (9) we derived the value

$$H=\frac{(u_0/u_{\max})^2}{4\pi t_{\max}}, \quad (10)$$

where u_0 – initial content of phosphorus in the formed boundary (surface) layer of the column, which is about 100% of the amount of phosphorus introduced; u_{max} – content of phosphorus in the portion of filtrate, where the maximum removal of phosphates with the eluate wave is recorded; tmax – time of recording of the partial volume with the maximum content of phosphorus. Next, we calculated the diffusion coefficient D, which determines the mobility of phosphorus compounds in the soils under study.

Results

The results of studies of filtration, sorption and mobility of soluble phosphates in the soils under study are graphic constructions of the Gaussian-type curves (Fig. 1–4), which reflect the dynamics of the phosphorus content in partial volumes of the filtrate of the eluate wave over time.

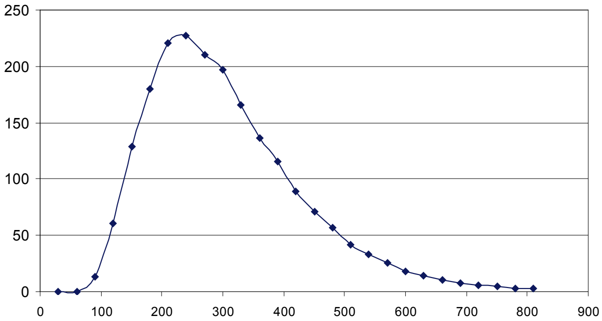

Fig. 1. Dynamics of phosphorus content in the partial filtrates (61g soil): on the abscissa axis – time время (minutes), on the ordinate axis – phosphorus content in the partial filtrates (mg)

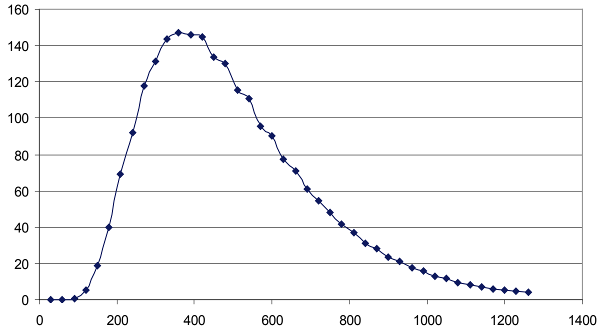

Fig. 2. Dynamics of phosphorus content in the partial filtrates (61g soil)

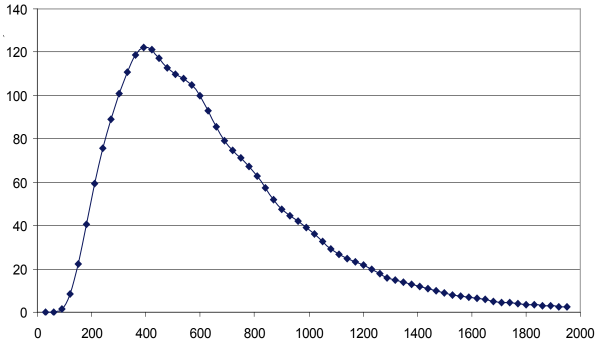

Fig. 3. Dynamics of phosphorus content in the partial filtrates (72g soil): on the abscissa axis – time (minutes, on the ordinate axis – phosphorus content in the partial filtrates (mg)

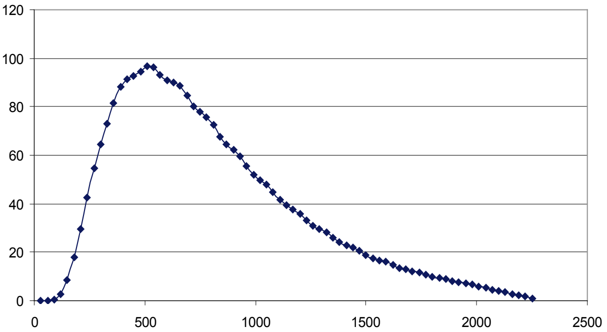

Fig. 4. Dynamics of phosphorus content in the partial filtrates (72g soil): on the abscissa axis – time (minutes), on the ordinate axis – phosphorus content in the partial filtrates (mg)

The results of calculations obtained when analyzing the graphic constructions based on experimental data are shown in Tables 5–7. Table 5 presents the indicators characterizing the movement of eluate wave as a whole. Tables 6 and 7, accordingly, show the leading edge of the eluate wave, i.e. the ascending part before the maximum and the descending part of the wave after the maximum. The indicators below served as the main characteristics given in tables:

– W, cm^3/min – rate of volume filtration of water through the column. This indicator depends on the granulometric composition of the soils under study and sum of absorbed bases.

– V, cm/min – linear speed of water flow through the column. The indicator is obtained with W ratio to the column area 38.46 cm^2.

– V', cm/min – linear speed of movement of the maximum of eluate wave of phosphorus in the column, calculated by the time of appearance of the maximum value of the phosphorus content in the partial sample. The value of V' is lower than the value of the linear speed of total flow of water V, which is filtered through the soil in the column, because of the permanent process of phosphates' sorption and desorption during their movement in the water flow.

– t, min – total filtration time, comprising time intervals of the appearance of the eluate wave maximum (t_1) and its attenuation (t_2) at the exit from the column. It depends on the granulometric composition and absorbed bases distributed in the soil.

– 1/h – dimensionless value inverse of the distribution coefficient, or the sorption index h. It shows how many times the amount of adsorbed phosphorus exceeds its content in the solution. It is the main indicator in the calculation of the absorbing capacity of the soil.

– H, cm^2/min – coefficient of mobility or diffusion of phosphorus compounds in the soils under study taking into account the sorption. It is calculated from the values of the maximum of eluate wave and the time of its appearance t_1 (for the frontal part of the wave) and the time from the appearance of the maximum to attenuation of the eluate wave t_2.

– D, cm^2/min – coefficient of mobility or diffusion of phosphorus compounds in the soils under study without taking into account the sorption. It is calculated from the values of H and h.

– v, mL – partial volume of the filtrate, that is, the volume of a discrete portion of filtrate obtained in 30 min. For each type of soil under study, discrete portions of filtrate in the fixed sampling time interval showed the same volume during the experiment.

– Σ v, mL – total volume of filtrate obtained for the entire filtration time, i.e. during the passage of ascending and descending parts of the eluate wave. The total volume of filtrate, as well as the partial volume, was different for each type of soil under study, which is associated with the varying granulometric composition of soils and sum of absorbed bases.

The tables include a complete set of indicators that determine both vertical and horizontal migration of phosphorus compounds in the soil.

Table 5
Filtration characteristics of the soils under study

Variant of experiment	Code of agro-group	*W*, cm^3/min	*V*, cm/min	*V'*, cm/min	*1/h*	*t*, min.	*Σv*, ml
1	61g	10.25	0.266	0.058	3.597	800	7995
2	61d	8.15	0.212	0.036	4.878	1170	9535
3	72g	7.45	0.194	0.031	5.319	1950	14527
4	72d	7.05	0.183	0.024	6.493	2220	15650

Table 6
Indicators of ascending part of the eluate wave

Variant of experiment	Code of agro-group	*H*, cm^2/min	*D*, cm^2/min	*v*, mL	*Σv*, mL	t_1, min
1	61g	0.083	0.379	307.5	2460	240
2	61d	0.066	0.388	244.5	2934	360
3	72g	0.085	0.540	223.5	3129	420
4	72d	0.077	0.575	211.5	3595	510

Table 7
Indicators of descending part of the eluate wave

Variant of experiment	Code of agro-group	*H*, cm^2/min	*D*, cm^2/min	*v*, m	*Σv*, ml	t_2, min
1	61g	0.037	0.169	307.5	5535	540
2	61d	0.023	0.137	244.5	6601	810
3	72g	0.023	0.148	223.5	11398	1530
4	72d	0.020	0.150	211.5	12055	1710

Discussion

Agrochemical indicators of the soils under study give a fairly complete characteristic of their basic physico-chemical properties, which generally determine the processes of sorption of soluble phosphates and their mobility. Firstly, it is necessary to assess the level of influence of mobile phosphates already present in the soils under study based on agrochemical indicators (Table 3).

In general, the content of mobile phosphates (P_2O_5) in the soils under study does not exceed 150 mg/kg; this value corresponds to 65.5 mg/kg of phosphorus (P) and is characteristic of chernozem soils (Nosko, 2018). When expressed in terms of a centimeter of the cross-sectional area of the column, it is 4.4 mg, and in relation to the formed boundary (surface) layer, it is about 0.17%. Therefore, in the process of movement of the eluate wave, the content of mobile phosphorus in the soil sample will have a minimal effect, which can be neglected. Regarding the sufficiently large amount of phosphorus incorporated into poorly soluble compounds (about 600 mg/kg), its influence on the results of the experiment will also be minimal for the reasons below.

Taking into account the weakly acidic reaction (pH 3.5–4.5) of the eluate wave (Santos et al., 2016), which is manifested already at the short distance of 2–3 cm from the formed boundary layer, as well as the short time of contact of the eluate wave and high constants of the product of solubility of hydroxylapatite and octacalcium phosphate pK 113.7 and 146.9, i.e. compounds that determine about 85% of the total phosphorus content in the soils under consideration, we can evaluate the level of phosphate injection into the solution of poorly soluble phosphorus compounds at approximately 3–4 % of the initial amount of phosphates on the column surface in the boundary layer. It is a negligible quantity.

The sorption of phosphorus compounds is the first stage of transition of mobile compounds of $H_2PO_4^-$ into poorly soluble compounds.

The main and the most informative indicator is h, the inverse value of which characterizes the displacement of equilibrium in the system "soil solution – solid phase" towards the solid phase, that is, it determines the sorption process. This indicator increases in the range of soils 61g–61d–72g–72d (Table 5) with the growing content of physical clay and sum of absorbed bases. It can be noted that these values indicate rather significant equilibrium displacement towards sorption and poorly soluble fraction of phosphates.

The key factor in the formation of poorly soluble fraction of phosphates is the factor of the sum of absorbed bases (Fig. 5).

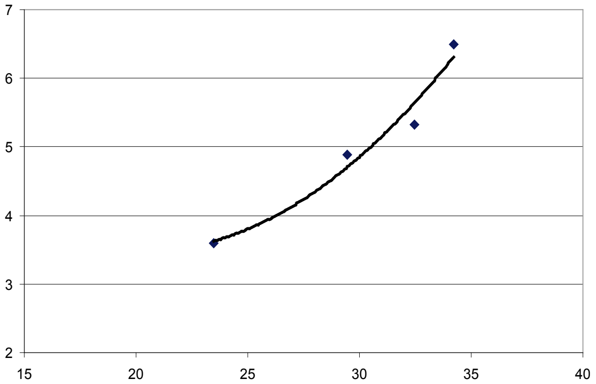

Fig. 5. Dependence of sorption coefficient on the sum of absorbed bases: on the abscissa axis – adsorbing capacity (mmol/100 g); on the ordinate axis – sorption coefficient (L/hg)

This is evidenced by the analysis of ratios of sorption coefficients (L/h) of the soils differing in mechanical composition and salinity. For example, the ratio of sorption coefficients of 61d medium loamy soil to 61g light loamy soil is 1.356, which is quite close to the ratio of physical clay content in these soils (1.249). For 72d and 72g medium and light loamy soils, these ratios are 1.221 and 1.283, respectively. Thus, the change in the physical clay content is proportionally reflected in the changing sorption coefficients. The similar analysis of the sum of absorbed bases shows that even slight changes in their content in saline soils lead to significant increase in sorption coefficients. At the ratio of the amount of absorbed bases of 72d and 72g soils being equal to 1.053, the ratio of their sorption coefficients was 1.221.

Our findings (Tables 6, 7) also make it possible to reveal the peculiarities of the transformation of diffusion coefficients H and D – mobility of phosphates during the movement of the eluate wave. It can be seen from the fact of asymmetry of graphic constructions, i.e. frontal part of the wave changes more dynamically compared to the next part. There is a significant, several times, decrease in the diffusion coefficients of the descending part of the wave compared to its ascending part, respectively, for 61g, 61d, 72g and 72d soils – 2.24, 2.87, 3.69 and 3.85 times. This phenomenon is associated with the successive transformation of phosphates – monocalcium phosphate $Ca(H_2PO_4)_2$ into dicalcium phosphate $CaHPO_4$. These compounds in their sequence reflect a decrease in the solubility of phosphates. Thus, in the presence of absorbed calcium in the soil, the most probable compound is dicalcium phosphate (Kovalenko, 2021). The mobile anion of orthophosphoric acid $H_2PO_4^-$ is rather quickly converted into this compound.

Valuable information can be obtained from graphic constructions (Fig. 1–4) regarding kinetic characteristics of the transformation of phosphates from the residue of orthophosphoric acid $H_2PO_4^-$, the molar content of which is usually equated with the phosphate potential. If we correlate the time of filtration of the descending part of the eluate wave with its frontal part, we get the following ratios for the soils under study: 1 – 2.25; 2 – 2.25; 3 – 3.64; 4 – 3.36. They indicate that phosphates in the soil pass into a state defined by the dynamic system "soil solution – monocalcium phosphate – dicalcium phosphate" during the entire time of filtration.

The convectional diffusion is largely related to the intensity of the flow, that is, to the volume velocity and total amount of solvent (water). In this aspect, an informative indicator is the total amount of water required for complete filtration of the phosphate introduced into the upper part of the column.

The evaluation characteristics that can be obtained from the total volume of filtrate (Table 5), i.e. the volume required for the complete conversion of phosphorus into solution in the dynamic system "soil solution – monocalcium phosphate – dicalcium phosphate", are of particular interest. The complete dissolution of 9.92 g of composition $Ca(H_2PO_4)_2/ CaHPO_4$ in the proportion of 60% and 40%, which corresponds to 7.908 g of $H_2PO_4^-$, i.e. the amount of phosphate anion of $H_2PO_4^-$ introduced in the column at the beginning of the experiment in the form of 5 mL of 85% orthophosphoric acid of density 1.88 g/mL, requires the availability of water for the soils under study: 1 – 7.99, 2 – 9.53, 3 – 14.53, 4 – 15.65 L. The obtained indicators allow us to adjust the rates of application of phosphate fertilizers in specific relation to the potential moisture content of the soil.

It should be noted that variations in the values of the required amount of solvent (water) in the main soils under study in Dnipropetrovsk region are quite significant – from 8 to15.5 liters. Most importantly, large volumes (14.5–15.5 L) are necessary in the presence of salinity in 72g and 72d soils. These estimates are useful in the calculations of the rates of phosphate fertilizer application for the planned crop yield, since a large part of the phosphate fertilizers will not be used in the conditions of the lack of moisture. For example, for the planned yield of wheat of 50 dt/ha, with the presence of 80–100 mg/kg of mobile phosphates in the soil, according to Chirikov, it is necessary under the balance charts to introduce into the arable horizon about 50 kg/ha of phosphate fertilizers (in terms of P_2O_5). In the averaged calculation, it is ~ 0.04 g/kg in 10 cm of the arable layer. According to our estimates, 61g and 61d soils require 21–29 mL of water to dissolve this amount of phosphate fertilizers, and 72g and 72d soils – about 39–43 mL in the upper arable horizon.

Considering the fact that at the moisture content of ~ 10–15% (according to long-term annual average data for April–May, 150–160 mm of moisture in one meter layer of the soil), taking into account the osmotic and matrix potentials, in particular, in salinized and alkali-affected soils, an effective indicator of soil moisture content will be approximately 80–100 mL/kg. With due regard for the summer dynamics of moisture loss from the soil, upon reaching the state of rupture of capillary bonds (pF 3.5) (Pogromska, 2020), the capillary moisture content in the soil is 30–35 mL/kg. Then the indicator of water needed to dissolve phosphate fertilizers in saline soils (39–43 mL) cannot be reached. In this case, phosphate fertilizers will not completely dissolve. Even if complete dissolution of phosphates occurs over a long period, then during this time they are additionally transformed into practically insoluble compounds of octacalcium phosphate and hydroxylapatite. Further evaluations should take into account the dynamics of water supply as a whole by phases of plant development during the growing season.

Therefore, the proposed method allows one to perform a quantitative assessment of the mobility of dissolved phosphates in soils. The temporal characteristics of transformation of the phosphate mobility in the process of convectional filtration in soils, found by experiment, can be used to evaluate the required level of water availability in soils for the effective use of phosphate fertilizers in the combination of calcium monophosphate and calcium diphosphate compounds.

Conclusion

The method of eluate wave allows one to evaluate, in a comprehensive manner and with sufficient accuracy, the main sorption characteristics, indicators of mobility and accordingly the availability of phosphates for plants in specific soils. Depending on the structure of salinization and the content of absorbed bases, phosphate sorption coefficients 1/h vary within 3.6–6.5 units, and mobility coefficients – from 0.15 to 0.57 cm^2/min.

Based on the above estimates of dynamic solubility, i.e. the required amount of water to dissolve the combined calcium phosphate/calcium diphosphate system, which is mostly matched by phosphate fertilizers (including combined ones), we may conclude that ordinary light and medium loamy chernozems at the average moisture content can provide satisfactory efficiency (of about 70–80%) of the use of phosphate fertilizers at the application rate of max. 40–45 kg/ha of active substance. At the average level of soil salinity along with steppe alkali soils (30–40%), the maximum rate of application of phosphate fertilizers is much lower and varies from 20 to 25 kg/ha of active substance.

The sum of absorbed bases is the key factor affecting the sorption coefficient of phosphorus compounds in the soil, that is, binding of phosphates during their filtration in the upper soil horizons. The sum of bases growing from 23.5 to 34.2 mmol/100 g leads to the increase in the sorption coefficient from 3.6 to 6.5. Thus, in the presence of even the average level of salinity, the amount of strongly bound phosphates almost doubles.

The estimates obtained in the paper allow one to optimize the rates of application of phosphate fertilizers towards their reduction, taking into account the factors of water availability and the level of salinity. Therefore, they give an opportunity to significantly increase the efficiency of use of phosphate fertilizers under conditions of lack of moisture in the chernozem soils of the Steppe zone of Ukraine.

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