

## The Influence of Chemical Amelioration on the Structure of the Phosphate Fund of Retisol of Western Polissia in Ukraine

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### ABSTRACT

The study of changes in the structure of the phosphate fund of retisol after two rotations of a 4-field field crop rotation under the influence of the introduction of dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) and limestone ( $\text{CaCO}_3$ ) flour in different doses before the start of the first rotation was carried out in the stationary experiment of the Institute of Agriculture of the Western Polissia of Ukraine. The dose of limestone materials is calculated on the basis of hydrolytic acidity (Hh) 2.80–2.97 mol/kg: for dolomite flour 0.5 Hh – 2.2 t/ha; 1.0 Hh – 4.7; 1.5 Hh – 6.7 t/ha; for limestone flour 1.0 Hh – 4.9 t/ha. The saturation of crop rotation with mineral fertilizers was  $\text{N}_{112}\text{P}_{87}\text{K}_{105}$ . The general background of the experiment was the annual application of the non-marketable part of the crop at a dose of 6.0 t/ha of biomass. The purpose of the work is to investigate the directionality of the transformation of the forms and different fractions of retisol phosphorus under the influence of liming against the background of systematic fertilization after the completion of the second crop rotation rotation. Research has established that under the influence of the introduction of meliorants, the share of mineral phosphorus compounds (P inorganic) fluctuated widely according to the experiment options (47.0 – 67.4% of P total), and organic – in the range of 28.5–37.5% P total. Liming against the background of fertilizer application also caused certain changes in the proportions between different forms of phosphorus. The main part (55.5–70.7%) of inorganic P is aluminum phosphates (Al-P) and iron phosphates (Fe-P). Liming with increasing doses of meliorants significantly ( $p = 0.05$ ) affected the reduction of the total share of Al-P and Fe-P compared to the control and application of only mineral fertilizers, and also contributed to a significant increase in the share of Ca-P calcium phosphates ( $p = 0.01$ ). At  $\text{pH}_{\text{KCl}}$  4.0–6.0, the content of P inorganic fractions was distributed in the order from maximum to minimum indicators: Al-P > Fe-P > P soluble > Ca-P. Neutralization of the acidity of the soil solution also contributed to a significant increase in the content of the soluble fraction of phosphorus (P soluble) to 4.9–5.4% of total P ( $p = 0.05$ ), and the level of availability of labile phosphorus compounds of the studied soil increased and was noted as high. The established features of the transformation of the phosphate pool in retisol under the influence of the introduction of chemical ameliorants indicate an increase in the share of bioavailable phosphorus compounds, significant changes in the conditions of phosphorus nutrition of crop rotation crops and a change in the functional stability of the agroecosystem in general.

**Keywords:** total phosphorus, forms and fractions of phosphorus, dolomite and limestone flour, fertilizer, acidity.

### INTRODUCTION

Agricultural production significantly affects the nutrient regime of anthropogenically modified soil, in particular, the content and transformation of phosphorus compounds. The use of fertilizers and the implementation of soil improvement measures contribute to soil cultivation with the

formation of a characteristic phosphate regime in it, different from natural analogues [Lun et al, 2017]. As a result of strong adsorption, rapid deposition and immobilization of phosphorus in inaccessible forms, accumulation of phosphorus-containing compounds in the soil is possible [Menezes-Blackburn et al., 2018]. Therefore, rational management of plant phosphorus

nutrition conditions requires an understanding of the chemical interaction of different forms of phosphorus in the soil, as this information is important for diagnosing and predicting its lability and bioavailability [Wierzbowska, 2020; Li Cuilan et al., 2021].

A significant part of the research on the phosphorus fund of the soils of Ukraine is devoted to the analysis of the state of the soil cover, mainly of the sod type of soil formation [Nosko 2017a, 2018; Khristenko et al., 2020; Miroshnychenko et al., 2021; Lopushniak, 2014].

However, issues related to the transformation of the phosphorus pool in retisols, which are characterized by certain features associated with increased acidity of the soil environment and the use of chemical amelioration, have been studied to a lesser extent, which led to our research.

It is known that the content of bioavailable phosphorus compounds largely reflects the general level of cultivation of retisols. The main source of replenishing the soil solution with mobile forms of phosphorus is its gross reserves, which are concentrated in the parent rock and phosphorus-containing organic compounds of the soil. Together with them, water-soluble compounds of phosphorus, which enter the soil with mineral fertilizers, play a significant role [Vasbieva et al., 2021; Lopushniak et al., 2022].

A feature of the transformation of phosphorus compounds in retisols is the chelation of iron (Fe), manganese (Mn) and aluminum (Al) and their subsequent fixation with the formation of insoluble compounds [Ikhajiagbe et al., 2020]. Solving the problem of phosphorus binding in retisols is possible by neutralizing the acidity of the soil solution through the application of chemical ameliorants that contain lime, which can significantly affect the bioavailability of nutrients in the soil, the growth and development of plants and, in general, the functional stability of the agroecosystem.

Applying lime is considered one of the most effective strategies for optimizing soil acidity, which can increase the availability of phosphorus in it [Qaswar et al., 2020]. During liming, the introduction of carbonate ( $\text{CO}_3^{2-}$ ) increases the pH of the soil environment, reduces the activity of aluminum oxides and the ability of their surfaces to hold phosphorus and, as a result, contributes to the increase in the bioavailability of phosphorus in the soil [Kisinyo et al., 2013]. However, Hinsinger (2001) points out that as the

pH of the soil increases, the solubility of Al and Fe phosphates increases, and the solubility of Ca phosphates decreases, with the exception of pH values above 8.0 units.

Therefore, phosphorus compounds in the soil are subject to dynamic transformations, the direction of which is partially determined by the change in physicochemical properties, in particular, the reaction of the soil environment caused by anthropogenic influence.

The presented study is devoted to the quantitative assessment of changes in different fractions of phosphorus in the retisols of the Western Polissia of Ukraine due to the application of mineral fertilizers and chemical meliorants in different rates.

## METHODOLOGY

The research was conducted in the stationary field experiment of the Institute of Agriculture of the Western Polissia of the Academy Agrarian of Sciences of Ukraine ( $50^{\circ}70'81''\text{N}$ ;  $26^{\circ}54'55''\text{E}$ ) during two rotations of a four-field crop rotation (2012–2019) on a typical soil for this soil and climate zone – Retisol (Albic Retisol (Arenic, Aric) [WRB, 2021]. The area of the sowing plot is  $99 \text{ m}^2$ , the accounting plot is  $50 \text{ m}^2$ , the repetition is three times, the placement is consecutive.

Crop rotation involved the following rotation of crops: winter wheat, corn for grain, spring barley, winter rapeseed. The general background in all variants of the experiment was the production of air-dry biomass of the non-marketable part of the crop: wheat and barley straw, corn and rape stalks and leaves, in an amount that averaged  $6.0 \text{ t/ha}$  per crop rotation. In all variants, except for the control, mineral fertilizers were applied in the form of ammonium nitrate, amphos, potassium chloride in appropriate doses: winter wheat –  $\text{N}_{120}^{\text{P}}\text{K}_{90}$ , corn for grain –  $\text{N}_{120}^{\text{P}}\text{K}_{120}$ , spring barley –  $\text{N}_{90}^{\text{P}}\text{K}_{90}$ , winter rapeseed –  $\text{N}_{120}^{\text{P}}\text{K}_{120}$ . The dose of mineral fertilizers was  $\text{N}_{112}^{\text{P}}\text{K}_{82}\text{K}_{105}$  per hectare of crop rotation area.

Doses of chemical meliorants (D) were determined by the hydrolytic acidity of the soil (Hh) according to the formula:

$$D (\text{t/ha}) = 1.5 \times Hh \quad (1)$$

For the calculation, the initial indicators of hydrolytic acidity of the soil of  $2.80\text{--}2.97 \text{ mol/kg}$  of soil were used in all the studied options.

Chemical ameliorants were introduced before the establishment of a stationary experiment in 2011, namely dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) and limestone ( $\text{CaCO}_3$ ) class A flour with the sum of Ca and Mg carbonates at least 90%. According to the level of hydrolytic acidity of the soil and the neutralizing capacity of the meliorant (carbonate content, %), the following amounts of dolomite flour were used in the experiment: 2.2 t/ha corresponded to 0.5 Hh of  $\text{CaMg}(\text{CO}_3)_2$ ; 4.7 t/ha – 1.0 Hh of  $\text{CaMg}(\text{CO}_3)_2$ ; 6.7 t/ha – 1.5 Hh of  $\text{CaMg}(\text{CO}_3)_2$ ; a dose of 1.0 Hh of  $\text{CaCO}_3$  corresponded to 4.9 t/ha of limestone flour.

Thus, the scheme of the experiment included the following options: 1. Control (without fertilizers); 2.  $\text{N}_{112}\text{P}_{82}\text{K}_{105}$  (NPK); 3. NPK +  $\text{CaMg}(\text{CO}_3)_2$  (0.5 Hh); 4. NPK +  $\text{CaMg}(\text{CO}_3)_2$  (1.0 Hh); 5. NPK +  $\text{CaMg}(\text{CO}_3)_2$  (1.5 Hh); 6. NPK +  $\text{CaCO}_3$  (1.0 Hh).

Soil samples were taken from the 0–20 cm layer of retisol. The average sample for analysis was prepared from five soil samples taken diagonally from each experimental plot at approximately the same distance. For laboratory analysis, soil samples were dried to an air-dry state and sifted through a sieve with a diameter of 0.25 mm.

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Indicators of the exchangeable acidity of the soil solution ( $\text{pH}_{\text{KCl}}$ ) were measured using a pH meter with a glass combined electrode in a suspension of 1M KCl at a ratio of soil: extractant of 1:2.5.

To determine available phosphorus compounds, samples were taken annually at the end of the growing season of field crops during two crop rotations (winter wheat, spring barley, winter rape – in July, corn for grain – in September). Determination of the content of phosphorus avail. was carried out by the Kirsanov method in an extract with 0.2 M HCl in the ratio of soil: extractant 1:5. The concentration of phosphorus in the filtrate was determined colorimetrically by the ascorbic method, using the red light filter of the photometer with a transmission length of 660 nm [Horodnyi et al., 2007; Murphy and Riley, 1962].

In order to analyze the change in the phosphate regime of the soil, samples were taken after the completion of the second rotation of crop rotation (2019).

The content of phosphorus in soil organic compounds (P org.) to be the ignition method of Saunders and Williams, which is based on the parallel determination of phosphorus in calcined at a temperature of 550 °C and uncalcined soil treated with 0.2 M with a solution of  $\text{H}_2\text{SO}_4$  in the ratio soil: extractant 1:50. The obtained suspensions were shaken for 2 hours, settled for 16–18 hours and filtered. In an aliquot of two solutions, phosphorus content was determined colorimetrically by the ascorbic method. The P org content was determined by the difference in the phosphorus content of the calcined (total content of phosphorus compounds – P tot.) and non-roasted (content of mineral phosphorus compounds – P in.) samples. in the soil [Soon and Hendershot, 2006].

The Chang-Jackson method [Chang and Jackson, 1957] was used to characterize the fractional composition of mineral compounds of phosphorus (P in.) in the soil, which is based on the sequential treatment of a sample of soil with different solvents, each of which extracts certain fractions of mineral phosphates in the soil ratio: solution 1:50.

Sequential phosphorus extraction schemes can be used to separate P in. into different fractions, including soluble phosphates (P sol.), aluminum phosphates (Al-P), iron phosphates (Fe-P) and calcium phosphates (Ca-P), according to differences in the binding of basic cations to orthophosphates [Yan et al., 2020].

Fractions P in. in soil samples was determined in the following sequence:

1. P soluble (P sol.) – by adding 50 ml of 1.0 M  $\text{NH}_4\text{Cl}$  to 1.0 g of soil, shaking for 30 min, centrifugation, filtering, measuring the content of P in the filtrate;
2. Al-P by shaking the residue from (1) in 50 ml of 0.5 M  $\text{NH}_4\text{F}$  for 1 h, centrifugation and filtration, then measuring the P content of the filtrate;
3. Fe-P by shaking the residue of (2) in 50 mL of 0.1 M NaOH for 2 h, settling for 16 h, shaking again for 2 h, centrifugation, and filtration. The P content in the filtrate was measured after acidification of the medium with 1.5 ml of concentrated  $\text{H}_2\text{SO}_4$  followed by filtration. After that, saturated NaCl solution was poured into the remaining soil, shaken for 15 min, centrifuged, the solution was deposited, and the soil was used for further analysis.
4. Ca-P by shaking the washed soil residue (3) with 50 ml of 0.25 M  $\text{H}_2\text{SO}_4$  for 1 h, centrifugation, filtration, measurement of P content in the filtrate.

Determination of P content in filtrates was carried out colorimetrically by the ascorbic method [Soon and Hendershot, 2006]. The content of residual fractions of phosphorus (P residual – P res.) was calculated as the difference between P tot. and the sum of the extracted phosphorus fractions (P sol., Al-P, Fe-P, Ca-P, P org.).

### Statistical analysis

The significance of experimental data was assessed on the basis of one-way analysis of variance (ANOVA) and Fisher's test (F-test) at  $p = 0.05$ . Regression analysis was used to determine changes in the exchangeable acidity of the soil solution ( $\text{pH}_{\text{KCl}}$ ) and different fractions of mineral phosphorus. Pearson's correlation analysis at the significance level  $p = 0.05$  and  $0.01$  was performed to determine the relationship between different fractions of phosphorus and  $\text{pH}_{\text{KCl}}$ . The analysis of indicators of availability of phosphorus compounds was carried out by the method of descriptive statistics at  $p = 0.05$  in the program Statistika 10.0.

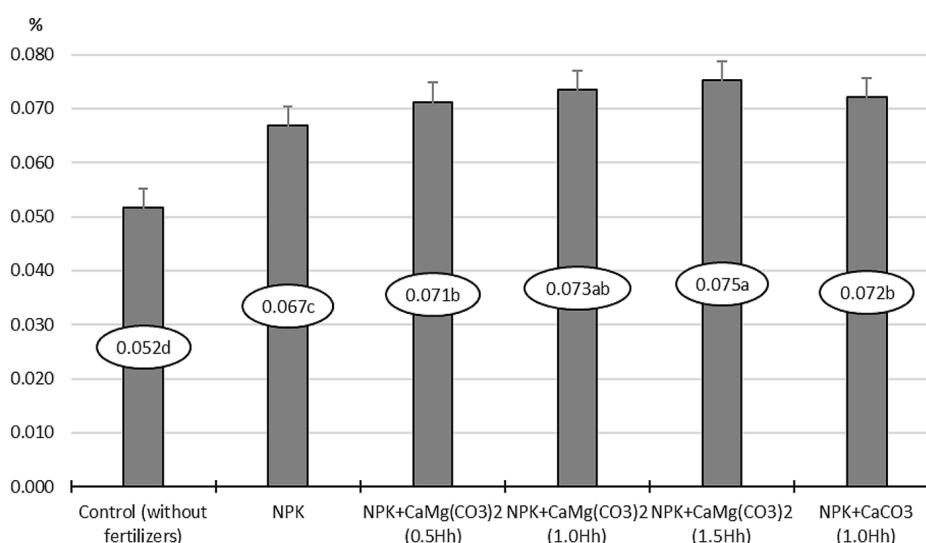
## RESULT AND DISCUSSION

Retisols are distinguished by a significantly lower total amount of phosphorus compounds (P tot.) compared to other types of soils common in Ukraine. In the upper layer of the studied soil, accumulation of P tot. can be

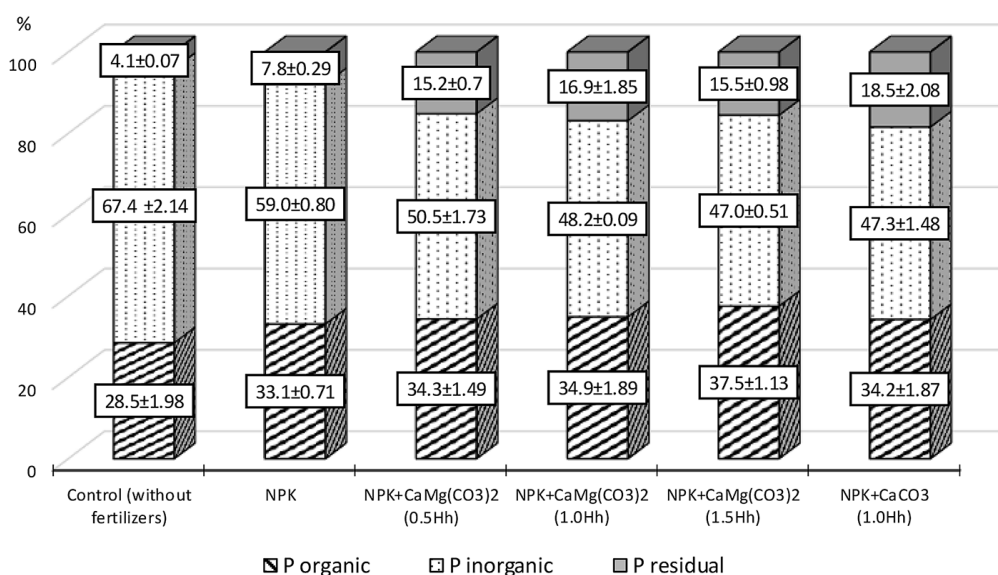
traced in the options where liming was carried out. Under such conditions, the effect on the P tot. content is more significant. Had 1.0 and 1.5 Hh doses of  $\text{CaMg}(\text{CO}_3)_2$ , although no significant difference between the introduction of such doses was established. Compared with these options, the indicators of P tot. in the control variant (without fertilizers and liming) decreased by 28.8–30.7%. Dynamics of P tot. content associated with the transformation of phosphorus compounds in the soil.

Phosphorus in the soil is in the composition of mineral and organic compounds, the ratio between which changes significantly during the systematic application of fertilizers to the cultivated crops during two rotations of crop rotation and liming, carried out before starting the experiment. This caused the differentiation of the content of various phosphorus compounds in the soil (Fig. 2).

Phosphorus total represented to a greater extent by mineral compounds: P in. (47.0–67.4% P tot.) > P org. (28.5–37.5% P tot.). The lowest content of P org. fixed in the control version – the ratio P in. : P org. is 2.36 : 1. Liming had a positive effect on the accumulation of P org. in the 0–20 cm soil layer. The use of 1.5 Hh dose of  $\text{CaMg}(\text{CO}_3)_2$  contributed to the reduction of the P in ratio. : P org. up to 1.25 : 1. However, the difference in the content of P org. for the introduction of limestone flour at a dose of 1.0 Hh (option 6) compared to dolomite flour at a dose of 0.5 and 1.0 Hh (options 3, 4) was statistically unreliable at  $p = 0.05$ .



**Figure 1.** Change in the total content of phosphorus compounds due to the application of fertilizers and chemical meliorants after the completion of the second rotation of crop rotation (2019). Values with the same letters have no statistical difference by  $p = 0.05$



**Figure 2.** Change in the ratio of phosphorus compounds (P) in different forms (P org., P in., P res.) due to the application of fertilizers and chemical meliorants, in % of phosphorus total

The conditions of phosphorus nutrition of agricultural crops are evaluated mainly by the content of its mineral compounds in the soil. The largest share of P in. from Phosphorus total – (67.4%) installed in the control variant. The introduction of mineral fertilizers contributed to a slight decrease of this indicator to 59.0%, but a significant decrease in the share of phosphorus mineral compounds from its total content relative to the control in the experimental conditions was established due to the effects of ameliorants. During liming of 0.5 Hh CaMg(CO<sub>3</sub>)<sub>2</sub> and 1.0 Hh CaCO<sub>3</sub>, the proportion of Phosphorus in. decreased according to the level of 50.5–47.3% of Phosphorus total. The smallest share of Phosphorus in. recorded after 1.5 Hh dose of CaMg(CO<sub>3</sub>)<sub>2</sub> – 47.0% of Phosphorus total.

It should be noted that although liming did not provide a significant difference between

indicators of the content of Phosphorus in. depending on the doses and types of meliorants at *p* = 0.05, in the conditions of the experiment, a significant dynamic of the content of phosphorus compounds associated with its various fractions was established, which affected the formation of the phosphorus regime of the soil.

Analysis of the content of different phosphorus fractions revealed a predominance of aluminum (Al-P) and iron (Fe-P) compounds in retisols (Table 1). Their total share in the variant without fertilizers was 94.0% of P in. Systematic application of mineral fertilizers after the completion of two rotations of crop rotation caused a quantitative predominance of Al-P fractions in the soil – 240.8 mg/kg of soil (46.6% of P total).

Liming with increasing doses of dolomite flour helped to reduce the total share of Al-P

**Table 1.** Fractional composition of mineral compounds of retisol phosphates after the completion of the second crop rotation (2019), mg/kg of soil

Variants	Fractions of mineral phosphates				Al-P/Fe-P
	P sol.	Al-P	Fe-P	Ca-P	
Control (without fertilizers)	11.4 <sup>f</sup>	222.9 <sup>b</sup>	104.6 <sup>b</sup>	9.2 <sup>df</sup>	2.1
NPK	19.2 <sup>e</sup>	240.8 <sup>a</sup>	124.0 <sup>a</sup>	10.2 <sup>f</sup>	1.9
NPK + CaMg(CO <sub>3</sub> ) <sub>2</sub> (0.5 Hh)	21.9 <sup>c</sup>	232.1 <sup>b</sup>	89.1 <sup>d</sup>	16.4 <sup>cd</sup>	2.6
NPK + CaMg(CO <sub>3</sub> ) <sub>2</sub> (1.0 Hh)	25.4 <sup>b</sup>	210.7 <sup>d</sup>	92.6 <sup>c</sup>	25.7 <sup>b</sup>	2.3
NPK + CaMg(CO <sub>3</sub> ) <sub>2</sub> (1.5 Hh)	27.9 <sup>a</sup>	201.3 <sup>e</sup>	85.3 <sup>e</sup>	38.9 <sup>a</sup>	2.4
NPK + CaCO <sub>3</sub> (1.0 Hh)	20.5 <sup>d</sup>	216.6 <sup>c</sup>	80.9 <sup>f</sup>	23.5 <sup>b</sup>	2.7
LSD <sub>05</sub>	1.30	9.22	1.39	0.97	

**Note:** values with the same letters are not statistically different at *p* = 0.05.

and Fe-P in the total phosphorus pool to 55.5–58.8% of P total. With an increase in the dose of  $\text{CaMg}(\text{CO}_3)_2$  from 0.5 to 1.5 Hh, the content of Al-P compounds decreased by 30.8 mg/kg of soil, Fe-P – by 3.8 mg/kg of soil.

At the same time, an increase in the amount of the fraction (Ca-P) due to the introduction of limestone materials into the soil was noted. In the options where liming was not performed (options 1 and 2), the share of Ca-P was at the level of 1.8–2.0% of P tot. and had no significant difference at  $p = 0.05$ . The use of 1.0 Nh doses of  $\text{CaMg}(\text{CO}_3)_2$  and  $\text{CaCO}_3$ , although it did not provide a significant difference between the indicators ( $p = 0.05$ ), but at the same time it contributed to an increase in the Ca-P content by 2.6–2.9 times compared to the control. The most significant effect on increasing the amount of Ca-P up to 7.5% of P tot. small dose of 1.5 Hh  $\text{CaMg}(\text{CO}_3)_2$  (option 5).

The transformation of the precipitated forms of phosphorus had a positive effect on the amount of the P sol. fraction. Neutralization of soil acidity after the completion of the second rotation of crop rotation to a pH level of 5.6–6.0 due to the introduction of 1.0 and 1.5 Hh doses of  $\text{CaMg}(\text{CO}_3)_2$  contributed to an increase in the proportion of the soluble fraction of phosphorus to 4.9–5.4% from P total.

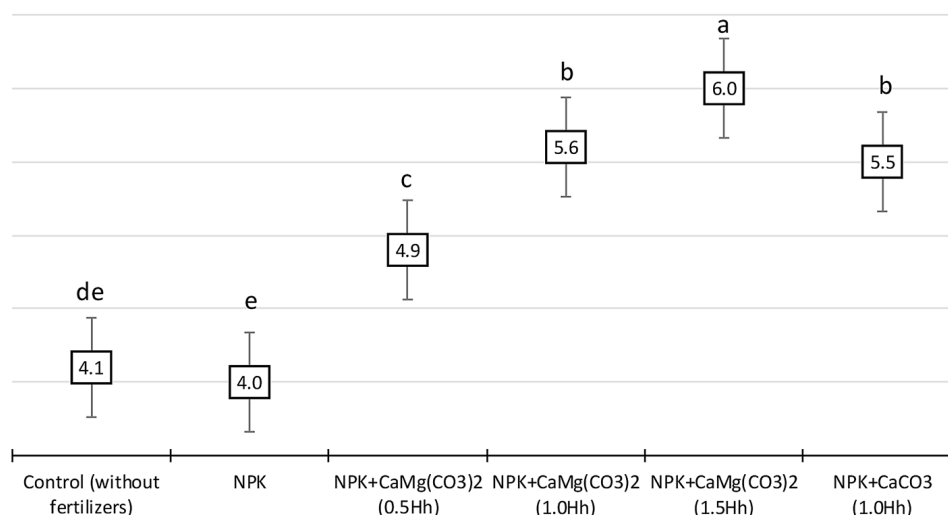
In options for the introduction of limestone materials (options 3–6), the accumulation of not only soluble phosphorus compounds (P sol.), but also residual insoluble fractions of phosphorus (P res.) was noted, especially in option 6, where a 1.0 Hh dose of  $\text{CaCO}_3$  was introduced. In this

version, the content of P res. was 18.4% of P tot., which was the highest indicator among all studied options. The lowest indicators of the content of this fraction – 20.9 mg/kg of soil (4.1% of P tot.) were noted in the control. Increasing the amount of P res. with the introduction of chemical meliorants may be associated with the reaction of phosphate ions with both the organic and mineral components of the soil with the formation of complexes inaccessible to plants [Ducoussou-Détréz et al., 2022].

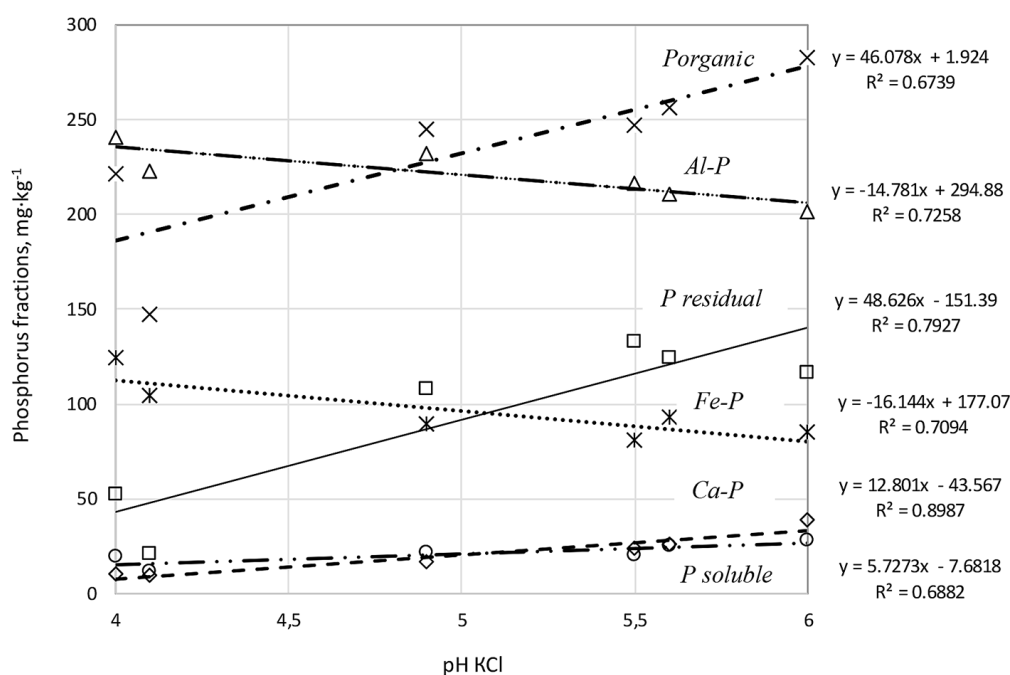
The introduction of limestone materials led to a statistically significant ( $p < 0.05$ ) increase in exchangeable acidity ( $\text{pH}_{\text{KCl}}$ ) of the studied soil compared to the control option and the option where only mineral fertilizers were applied (Fig. 3).

At the application dose of 1.5 Hh of  $\text{CaMg}(\text{CO}_3)_2$ , the  $\text{pH}_{\text{KCl}}$  index increased from 4.0 to 4.1 to 6.0 units. There was no significant difference in the effect of dolomite  $\text{CaMg}(\text{CO}_3)_2$  and limestone  $\text{CaCO}_3$  flour on the dynamics of  $\text{pH}_{\text{KCl}}$  ( $p = 0.05$ ). The relationship between indicators of exchange acidity and fractions of mineral phosphorus (P in.) in the soil is reflected in the regression equation (Fig. 4), where  $x$  determines the indicator of  $\text{pH}_{\text{KCl}}$  of the soil, and  $y$  – the change in the content of fractions of mineral phosphorus in the soil of the studied options. The slope of the regression equation shows the change in the concentration of the phosphorus fraction (mg/kg of soil) per unit increase or decrease in the reaction of the soil solution (pH).

Regression analysis of the content of different fractions of phosphorus mineral compounds and the level of exchangeable acidity of the soil



**Figure 3.** Change in the  $\text{pH}_{\text{KCl}}$  indicator of retisol at the end of the second rotation of the field crop rotation. Values with the same letters have no statistical difference by  $p = 0.05$



**Figure 4.** Change in the fractional composition of phosphorus compounds depending on the pH<sub>KCl</sub> index of retisol

solution showed that the change in the reaction of pH<sub>KCl</sub> in the range of 4.0 – 6.0 units. accordingly, the doses of limestone materials had a strong direct relationship with the Ca-P content ( $R^2 = 0.90$ ), P res. ( $R^2 = 0.79$ ), P sol. ( $R^2 = 0.69$ ) and inversely with the content of Al-P ( $R^2 = 0.73$ ) Fe-P ( $R^2 = 0.71$ ) in the 0 – 20 cm soil layer. From the presented multiple regression equations, it becomes obvious that an increase in the content of calcium phosphates and a decrease in the content of aluminum and iron phosphates contributes to an increase in the pH indicator, that is, a decrease in the content of H<sup>+</sup> ions in the soil solution.

In the studied soil, mobile phosphorus compounds (P avail.) were determined by the Kirsanov method, which is widely used in agrochemical practice of Ukraine and

is recommended for determining available phosphorus compounds in the arable (0–20 cm) layer of sod-podzolic soils [Khristenko, 2020; Nosko, 2017b]. According to the scale of availability of soil phosphorus compounds (P avail.), established for the Kirsanov method, the phosphorus content in the soil was characterized by a high level of availability (Table 2).

Doses of 0.5 and 1.0 Hh of CaMg(CO<sub>3</sub>)<sub>2</sub> and 1.0 Hh of CaCO<sub>3</sub> on the effect on the content of P avail. in the arable (0 – 20 cm) soil layer, there was no statistical difference ( $p = 0.05$ ). The highest content of P avail. on average, for the studied period, the dose of CaMg(CO<sub>3</sub>)<sub>2</sub> was set for 1.5 Hh.

To assess the relationship between pH indicators, the content of phosphorus fractions

**Table 2.** The content of labile phosphorus compounds (P avail.) in retisols depending on the application of fertilizers and chemical meliorants, mg/kg of soil (average for 2012–2019)

Variants	M+m	Min.	Max.	SD	V, %	S, %
Control (without fertilizers)	169.6 <sup>a</sup> +6.01	163.6	175.9	4.85	2.86	1.01
NPK	187.9 <sup>c</sup> +3.87	173.1	198.9	10.9	5.80	2.06
NPK + CaMg(CO <sub>3</sub> ) <sub>2</sub> (0.5 Hh)	196.5 <sup>b,c</sup> +5.18	175.2	217.0	14.7	7.48	2.64
NPK + CaMg(CO <sub>3</sub> ) <sub>2</sub> (1.0 Hh)	201.3 <sup>b</sup> +5.21	181.5	223.4	14.8	7.35	2.59
NPK + CaMg(CO <sub>3</sub> ) <sub>2</sub> (1.5 Hh)	216.8 <sup>a</sup> +6.04	184.8	237.5	17.1	7.89	2.79
NPK + CaCO <sub>3</sub> (1.0 Hh)	200.9 <sup>b</sup> +5.11	177.4	220.5	14.5	7.22	2.54
LSD <sub>05</sub>	13.4					

**Note:** values with the same letters do not have a statistical difference at  $p = 0.05$ ; M+m – arithmetic mean + deviation from the mean, Min. – minimum value, Max. – maximum value, SD – standard deviation, V – coefficient of variation, S – relative error.

**Table 3.** Pearson's correlation between  $\text{pH}_{\text{KCl}}$  and fractions of phosphorus compounds over the years of research

Parameter	pH	P organic	P soluble	Al-P	Fe-P	Ca-P	P residual
P organic	0.82*						
P soluble	0.83*	0.97**					
Al-P	-0.85*	-0.46	-0.54				
Fe-P	-0.84*	-0.53	-0.49	0.71			
Ca-P	0.95**	0.81*	0.85*	-0.87*	-0.7		
P residual	0.89*	0.88*	0.82*	-0.54	-0.79	0.75	
P available	0.89*	0.98**	0.96**	-0.61	-0.62	0.91**	0.87*

**Note:** the correlation is significant at the probability levels \* $p = 0.05$ , \*\* $p = 0.01$ .

and the amount of its mobile compounds in the arable layer of the soil, the Pearson correlation coefficient was calculated (Table 3).

A close correlation was established between  $\text{pH}_{\text{KCl}}$  and Ca-P at  $p = 0.01$  and other fractions of the phosphate pool at  $p = 0.05$ . That is, increasing doses of calcareous materials due to a change in the exchangeable acidity of the soil contributed to a decrease in the content of Al-P and Fe-P fractions and led to an increase in the content of other fractions, including P avail. Comparison of indicators P org. showed a positive correlation with P sol. and P avail. for  $p = 0.01$ .

According to the conducted research, together with the content of P org. other soil fractions – Ca-P (for  $p = 0.01$ ) also had a certain contribution to the formation of available phosphorus compounds determined by the Kirsanov method.

The phosphate fund of retisols is represented by various forms of organic (P org.) and inorganic (P in.) compounds that undergo constant transformation depending on dynamic changes in the physical, biological, and chemical characteristics of the soil environment [Bindraban et al., 2020]. Organic phosphorus can be released during mineralization carried out by soil organisms and plant roots in combination with phosphatase secretion. These processes are significantly influenced by humidity, temperature, physicochemical properties of the soil and pH of the soil environment, and the supply of organic matter [Liu et al., 2013]. According to researchers [Jokubauskaite et al., 2015; Chulo et al., 2022], the content of P org. decreases with the use of increasing doses of lime, provided there is no additional source of organic matter entering the soil. In the studies of Kiflu et al. (2017) decrease in the amount of P org. occurs only when the pH index increases to a neutral level in conditions where the microbiological activity of the soil increases. According to Guo Z. et al. (2018), the

return of straw to the soil by 37–43% contributed to an increase in the P org content. compared to the option of applying only mineral fertilizers.

In our research, the combination of annual soil application of 6.0 t/ha of post-harvest residues, application of mineral fertilizers at the saturation of crop rotation  $\text{N}_{112}\text{P}_{87}\text{K}_{105}$  and liming led to an increase in the P org. content compared to the control variant. However, although significant changes in the content of this indicator in the 0–20 cm soil layer were established only after liming 1.5 Hh  $\text{CaMg}(\text{CO}_3)_2$ . At the same time, other doses and types of limestone materials did not provide a significant difference in the content of P org. in the soil compared to the option without fertilization.

Phosphorus in the soil, it can be represented by mineral compounds of iron and aluminum hydroxides, be included in the composition of primary and secondary minerals of soil-forming rocks. At a soil pH below 5.5, phosphorus is precipitated by  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  ions, while at a pH above 7, it is precipitated by  $\text{C}^{2+}$  ions [Penn et al., 2019]. Researchers note that in an acidic soil environment, the predominance of Al-P and Fe-P in the composition of phosphorus mineral compounds is associated with the presence of oxides and hydroxides of aluminum and iron with a large specific surface, capable of providing enhanced adsorption [Kiflu et al., 2017; Gupta et al., 2020]. Such fractions of fixed phosphorus are not available for plant nutrition [Patidar et al., 2019]. The specified regularity is also preserved in the researched retisol: at  $\text{pH}_{\text{KCl}}$  4.0–6.0, the content of fractions of phosphorus mineral compounds was distributed from the maximum to the minimum indicators in the following order: Al-P > Fe-P > P soluble > Ca-P.

In our experiment, increasing the dose of dolomite flour from 0.5 Hh (2.2 t/ha) to 1.5 Hh (6.7 t/ha) contributed to a decrease in the content



of Al-P + Fe-P by 8.7–39, 5 mg/kg of soil compared to the option where only mineral fertilizers were applied. According to Quiroga et al. (2017), a similar pattern is possible due to the action of limestone materials to reduce the content of exchangeable  $\text{Al}^{3+}$  by replacing it with  $\text{Ca}^{2+}$ , as well as soluble  $\text{Al}^{3+}$  by precipitation with hydroxyl anions, which are formed as a result of the hydrolysis of calcium carbonates in the soil solution. According to the research results, the content of the Al-P fraction had a significant inverse relationship with the content of the Ca-P fraction ( $R^2 = -0.87$ ,  $p = 0.05$ ) according to the test options.

According to Lopushnyak (2014), the ratio of the content of the aluminum phosphate fraction to the iron phosphate fraction affects the ability of the specified transition. Since in the equilibrium system tightly bound compounds (iron phosphates) prevail over less tightly bound ones (aluminum phosphates), an increase in the proportion of aluminum phosphates indicates a higher availability of mineral phosphorus compounds to plant root systems. For the studied soil, where the content of Al-P prevails over Fe-P more than twice, the indicators of the content of mobile phosphorus compounds are quite stable at  $5.0 < V\%$  (coefficient of variation)  $< 8.0$ , while in the control without fertilizers there are with a high level of stability  $V\% = 2.86$ . Simonsson M. et al. (2018) in a plant phosphorus uptake study showed that liming increases the solubility of fertilizer-applied phosphorus decades after liming.

According to Pavlichenko (2021), the annual long-term application of some mineral fertilizers replenishes the level of gross phosphorus compounds, but the content of its mobile forms is significantly inferior to their application against the background of liming. The noted changes in the content of available phosphorus compounds (P avail.) in the arable layer of the soil due to doses of limestone materials fully correspond to the indicated trend. The difference between these indicators according to the variants of the experiment is confirmed by statistical calculations ( $\text{LSD}_{0.05} = 13.4$ ). At the same time, a decrease in the content of P tot. and P avail. in the soil in the absence of liming and systematic application of fertilizers is consistent with the results of other studies [Appelhans et al., 2020; Mahmood et al., 2020; Cade-Menun, 2022].

## CONCLUSIONS

In the conditions of the Western Polissia of Ukraine, the use of dolomite  $\text{CaMg}(\text{CO}_3)_2$  and limestone  $\text{CaCO}_3$  flour on retisols before the start of the first and second rotation of a four-field field crop rotation with saturation with mineral fertilizers  $\text{N}_{112}\text{P}_{87}\text{K}_{105}$  and annual earnings of an average of 6.0 t/ha of by-product biomass significantly affects the total content of phosphorus, the fractional composition of its compounds and the formation of the phosphate regime of the soil.

An increase in the dose of one-time application of dolomite flour from 2.2 to 6.7 t/ha leads to an increase in the content of total phosphorus in the arable layer of the soil by 5.4%. However, equivalent amounts of  $\text{CaMg}(\text{CO}_3)_2$  and  $\text{CaCO}_3$  (dose 1.0 Hh) do not provide a statistically significant difference ( $p = 0.05$ ) in terms of the effect on increasing the content of total phosphorus in the soil.

In the composition of the total phosphorus fund of the soil, the share of mineral phosphorus compounds (P in.) outweighs the share of organic phosphorus compounds (P org.). However, with the introduction of chemical meliorants, the share of organic phosphorus compounds increases.

The main part is 81.1–94.1% P in. represented by phosphorus associated with aluminum (Al-P) and iron (Fe-P) cations. The introduction of limestone materials contributes to an increase in the proportion of calcium phosphates (Ca-P) and a decrease in aluminum phosphates (Al-P) and iron phosphates (Fe-P) with a statistically significant increase in  $\text{pH}_{\text{KCl}}$  from 4.0 to 6.0 ( $p = 0.05$ ) after completion of the second crop rotation. At  $\text{pH}_{\text{KCl}}$  4.0–6.0, the content of fractions of phosphorus mineral compounds (P in.) is distributed in order from maximum to minimum indicators:  $\text{Al-P} > \text{Fe-P} > \text{P soluble} > \text{Ca-P}$ .

Neutralization of the acidity of the soil solution also contributes to a significant increase in the content of soluble phosphorus compounds (P soluble) ( $p = 0.05$ ). Research has established a high correlation between  $\text{pH}_{\text{KCl}}$  and Ca-P ( $p = 0.01$ ) and other fractions of the phosphate pool ( $p = 0.05$ ). Compared to the control, an increase in soluble P was also noted in the 0–20 cm soil layer due to the application of meliorants, but this effect is significant only at the highest doses of lime application.

The established regularities of changes in the phosphate fund in retisols indicate the extremely important role of lime application, in particular in the form of dolomite flour ( $\text{CaMg}(\text{CO}_3)_2$ ), for optimizing the distribution of forms and fractions of phosphorus compounds in the soil and improving the regime of phosphorus nutrition of field crops.

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## REFERENCES

- Appelhans S., Carciochi W., Correndo A., Gutierrez Boem F., Salvagiotti F., Garcia F.O. et al. 2020. Predicting Soil Test Phosphorus Decrease in Non-P-fertilized Conditions. *Eur. J. Soil Sci.*, 72, 264–254. <https://doi.org/doi:10.1111/ejss.12946>
- Bindraban P.S., Dimkpa C.O., Pandey R. 2020. Exploring phosphorus fertilizers and fertilization strategies for improved human and environmental health. *Biol Fertil Soils.*, 56, 299–317. <https://doi.org/10.1007/s00374-019-01430-2>.
- Cade-Menun B.J. 2022. Changes in Soil Phosphorus Pools in Long-Term Wheat-Based Rotations in Saskatchewan, Canada With and Without Phosphorus Fertilization. *Span. J. Soil Sci.*, 12, 10737. <https://doi.org/doi:10.3389/sjss.2022.10737>
- Chang S.C., Jackson M.L. 1957. Fractionation of soil phosphorus. *Soil Sci.*, 84, 133–144. <https://doi.org/10.1097/00010694-195708000-00005>.
- Chulo F., Laekemariam F., Kiflu A., Gidago G., Getaneh L. 2022. Soil Phosphorus Fractions and Their Quantity in Acidic Luvisols under Lime Rates in Ethiopia. *Communications in Soil Science and Plant Analysis*, 54(3), 1–15. <https://doi.org/10.1080/00103624.2022.2112214>
- Ducousso-Détrez A., Fontaine J., Lounès-Hadj Sahraoui A., Hijri M. 2022. Diversity of Phosphate Chemical Forms in Soils and Their Contributions on Soil Microbial Community Structure Changes. *Microorganisms*, 10(3), 609. <https://doi.org/10.3390/microorganisms10030609>
- Guo Z., Liu H., Hua K., Wang D., He C. 2018. Long-term straw incorporation benefits the elevation of soil phosphorus availability and use efficiency in the agroecosystem. *Spanish Journal of agricultural research*, 16(3), 1101–1101. <https://doi.org/10.5424/sjar/2018163-12857>
- Gupta A., Maheshwari A., Khanam R. 2020. Assessment of phosphorus fixing capacity in different soil orders of India. *Journal of Plant Nutrition*, 43(15), 2395–2401. <https://doi.org/10.1080/01904167.2020.1771585>
- Hinsinger P. 2001. Bioavailability of soil inorganic P in the rhizosphere as affected by root-induced chemical changes: A review. *Plant and Soil*, 237, 173–195. <https://doi.org/10.1023/A:1013351617532>
- Horodniy M.M., Lisoval A.P., Bykin A.V. et al. 2007. *Agrochemical analysis*. Kyiv: Aristei, 624.
- Ikhajiagbe B., Anoliefo G., Rackelmann F. et al. 2020. Major phosphorus in soils is unavailable, yet critical for plant development. *Notulae Scientia Biologicae*. 12(3), 500–535. <https://doi.org/10.15835/nsb12310672>
- IUSS Working Group WRB (2022). World Reference Base for Soil Resources. International soil classification system for naming soils and creating legends for soil maps. 4th edition. International Union of Soil Sciences (IUSS), Vienna, Austria. <https://www3.ls.tum.de/boku/wrb-working-group/documents/wrb-2022/>
- Jokubauskaite I., Karcauskiene D., Antanaitis S., Mazvila J., Slepeliene A., Koncius D., Piaulokaite-Motuziene L. 2015. The distribution of phosphorus forms and fractions in Retisol under different soil liming management. *Zemdirb Agric.*, 102(3), 251–256. <https://doi.org/10.13080/z-a.2015.102.032>
- Khristenko A.O. 2020. Theoretical problems of the methodology of balance assessment of the cycle of macroelements in the “fertilizer-soil-plant” system. *Agrochemistry and Soil Science*, 90, 47–56. <https://doi.org/10.31073/acss90-05>.
- Kiflu A., Beyene S., Jeff S. 2017. Fractionation and availability of phosphorus in acid soils of Hagereselam, Southern Ethiopia under different rates of lime. *Chem. Biol. Technol. Agric.*, 4(21). <https://doi.org/10.1186/s40538-017-0105-9>
- Kisinyo P.O., Othieno C.O., Gudu S., Okalebo J.R., Opala P.A. 2013. Immediate and residual effects of lime and phosphorus fertilizer on soil acidity and maize production in Western Kenya. *Experimental Agriculture*, 50, 128–143. <https://doi.org/10.1017/S0014479713000318>
- Li C., Zhang P., Zhang J., Zhu P., Wang L. 2021. Forms, transformations and availability of phosphorus after 32 years of manure and mineral fertilization in a Mollisol under continuous maize cropping. *Archives of Agronomy and Soil Science*, 67(9), 1256–1271. <https://doi.org/10.1080/03650340.2020.1787385>
- Liu Z.P., Shao M.A., Wong Y.Q. 2013. Spatial patterns of soil total nitrogen and soil total phosphorus across

- the entire Loess Plateau region of China. *Geoderma*, 197–198, 67–78. <http://dx.doi.org/10.1016/j.geoderma.2012.12.011>
19. Lopushniak V.I. 2014. Changing fractions mineral phosphorus in dark-gray podzolic soil under various fertilization systems. *Bulletin of Agricultural Science*, 11, 12–15. [https://agrovisnyk.com/oldpdf/visnyk\\_11\\_2014.pdf](https://agrovisnyk.com/oldpdf/visnyk_11_2014.pdf)
  20. Lopushniak V., Hrytsuliak H., Gamayunova V., Kozan N., Zakharchenko E., Voloshin Y., Kotsyubynska Y. 2022. A Dynamics of Macro Elements Content in Eutric Podzoluvisols for Separation of Wastewater under Jerusalem Artichokes. *Journal of Ecological Engineering*, 23(4), 33–42. <https://doi.org/10.12911/22998993/146268>
  21. Lun F., Liu J., Ciais P., Nesme T., Chang J., Wang R., Goll D., Sardans J., Peñuelas J., Obersteiner M. 2018. Global and regional phosphorus budgets in agricultural systems and their implications for phosphorus-use efficiency. *Earth Syst. Sci. Data*, 10, 1–18. <https://doi.org/10.5194/essd-10-1-2018>, 2018
  22. Mahmood M., Tian Y., Ma Q., Ahmed W., Mehmood S., Hui X., Wang Z. 2020. Changes in Phosphorus Fractions and Its Availability Status in Relation to Long Term P Fertilization in Loess Plateau of China. *Agronomy*, 10(11), 1818. <https://doi.org/10.3390/agronomy10111818>
  23. Miroshnychenko M., Khristenko A., Hladkikh Ye. 2021. 50-year dynamics of the content of moving compounds of nitrogen, phosphorus and potassium in degraded chernozem according to the stationary field experiment. *Bulletin of Agricultural Science*, 8(821), 5–14. <https://doi.org/10.31073/agrovisnyk202108-01>
  24. Murphy J., Riley J.P. 1962. A Modified Single Solution Methods for the Determination of Available Phosphate in Natural Water. *Analytica Chimica Acta*, 27, 31–36. [http://dx.doi.org/10.1016/S0003-2670\(00\)88444-5](http://dx.doi.org/10.1016/S0003-2670(00)88444-5)
  25. Nosko B.S. 2017a. Modern problems of phosphorus in farming agriculture and ways of their solution. *Bulletin of Agricultural Science*, 6(95), 5–12. <https://doi.org/10.31073/agrovisnyk201706>
  26. Nosko B.S. 2017b. To the issue on the formation of the phosphate soil fund. *Agrochemistry and Soil Science*, 86, 87–92. [http://agrochemsoilsci.org/ACSS\\_no86\\_full\\_text.pdf](http://agrochemsoilsci.org/ACSS_no86_full_text.pdf)
  27. Nosko B.S. 2018. Natural and anthropogenic evolution of the phosphate fund for soils in Ukraine. *Agrochemistry and Soil Science*, 87, 92–99. [http://agrochemsoilsci.org/ACSS\\_no87\\_full\\_text.pdf](http://agrochemsoilsci.org/ACSS_no87_full_text.pdf)
  28. Ojo A.O., Adetunji M.T., Okeleye K.A., Adejuyigbe C.O. 2015. Soil Fertility, Phosphorus Fractions, and Maize Yield as Affected by Poultry Manure and Single Superphosphate. *International Scholarly Research Notices*, 10, 616213. <https://doi.org/10.1155/2015/616213>
  29. Patidar J., Sharma Y.M., Tagore G.S. 2019. Phosphorus fractions in contrasting soil Orders in Central India. *Int. J. Curr. Microbiol. Appl. Sci.*, 8, 3050–3059. <https://doi.org/10.20546/ijcmas.2019.801.325>
  30. Pavlichenko A. 2021. Influence of different fertilization and chemical recruitment systems on the phosphorus regime of gray forest soil. *Agroecological journal*, 4, 131–138. <https://doi.org/10.33730/2077-4893.4.2021.252966>
  31. Penn C.J., Camberato J.J. 2019. A Critical Review on Soil Chemical Processes that Control How Soil pH Affects Phosphorus Availability to Plants. *Agriculture*, 9(6), 120. <https://doi.org/10.3390/agriculture9060120>
  32. Qaswar M., Dongchu L., Jing H. et al. 2020. Interaction of liming and long-term fertilization increased crop yield and phosphorus use efficiency (PUE) through mediating exchangeable cations in acidic soil under wheat–maize cropping system. *Scientific Reports*, 10(19828). <https://doi.org/10.1038/s41598-020-76892-8>
  33. Quiroga M.J., Olego M.Á., Sánchez-García M., Medina J.E., Visconti F., Coque J.J.R., Garzón Jimeno J.E. 2017. Effects of liming on soil properties, leaf tissue cation composition and grape yield in a moderately acid vineyard soil. Influence on must and wine quality. *OENO One*, 51(4), 343. <https://doi.org/10.20870/oeno-one.2017.51.4.2039>
  34. Simonsson M., Östlund A., Renfjäll L., Sigtryggsson C., Börjesson G., Kätterer T. 2018. Pools and solubility of soil phosphorus as affected by liming in long-term agricultural field experiments. *Geoderma*, 315, 208–219. <https://doi.org/10.1016/j.geoderma.2017.11.019>
  35. Soon Y.K., Hendershot W.H. 2006. Methods of Soil Analysis. III Soil Chemical Analyses. Chapter 24 Total and Organic Phosphorus. By Taylor & Francis Group, LLC. [https://www.niordc.ir/uploads/86\\_106\\_Binder2.pdf](https://www.niordc.ir/uploads/86_106_Binder2.pdf)
  36. Vasbieva M.T., Zavyalova N.E. 2021. Phosphate regime of sod-podzolic soil in natural and agrophytoce-noses. *Dokuchaev Soil Bulletin*, 107, 92–115. <https://doi.org/10.19047/0136-1694-2021-107-92-115>
  37. Wierzbowska J., Sienkiewicz S., Zalewska M. et al. 2020. Phosphorus fractions in soil fertilised with organic waste. *Environ Monit Assess.*, 192, 315. <https://doi.org/10.1007/s10661-020-8190-9>
  38. Yan X., Yang W., Chen X., Wang M., Wang W., Ye D., Wu L. 2020. Soil Phosphorus Pools, Bio-availability and Environmental Risk in Response to the Phosphorus Supply in the Red Soil of Southern China. *Int J Environ Res Public Health.*, 17(20), 7384. <https://doi.org/10.3390/ijerph17207384>