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N:P ratio diagnostics in arable soils of the Left Bank Forest Steppe of Ukraine

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Goal. Determination of N:P ratios in soil, fertilizers and plants under different conditions of moisture supply for further development of climate-oriented crop fertilization systems.

Methods. The research was carried out on a soil-agrochemical polygon with an area of 24 hectares during 2018-2020, in a temporary field experiment in areas with different levels of moisture supply (2021), as well as in a stationary field experiment that was started since 1969 on the territory of the SE "DG Grakivske" NSC "ISSAR named after O. Sokolovsky" (Kharkiv region). The soil cover of the experimental plots is dominated by chernozem podzolized heavy loamy. The content of mobile forms of phosphorus and potassium in the soil was determined after extraction of 0.5 n CH_3COOH using the Chirykov method, nitrate nitrogen photometrically with disulfophenolic acid, ammonium nitrogen photometrically with Nessler's reagent. NPK content in plants was determined after ashing with a mixture of sulfuric and perchloric acid. **Results.** Stoichiometric regulation of N and P availability under conditions of weather and climate fluctuations and increased deficiency of mineral fertilizers is an important direction for improving fertilizer efficiency, stabilizing high levels of field crop yields, and predicting biophilic element cycles in the future. On the territory of the polygon with an area of 24 hectares, separate locations were found with a significantly higher N:P ratio in the arable layer due to an increase in the concentration of mineral nitrogen, the location of which coincided with the areas of soil moisture accumulation (r = 0.52-0.55). Within the soil areas, which differ in moisture conditions, a positive correlation was determined between the indicators of the $N:P_2O_5$ ratio in the soil and its moisture supply (r=0.49-0.53). The positive effect of adjusting this indicator on soybean yields has also been proven. On the research plot with the best moisture conditions

before sowing, the highest soybean grain yield was obtained at $N_{180}P_{60}K_{60}$ fertilizer rates, and on the plot with the worst moisture reserves - at $N_{120}P_{60}K_{60}$.

Conclusions. The regulation of the $N:P_2O_5$ ratio in the soil through the management of its nutritional status, that is, through the application of various doses and ratios of NPK, taking into account the level of soil moisture supply, affects the yield of crops, as well as the stoichiometry of nutrients in plants. The optimal ratios of N:(PK) for growing soybeans in the composition of fertilizers and in the soil on research plots with different levels of moisture supply were determined. An expansion of the N:P ratio in the main and by-products of field crops in more humid years has been established.

Key words: *nutritional balance, stoichiometry, nitrogen, phosphorus, fertilizer efficiency, moisture conditions.*

Introduction.

The progressive increase in the amount of fertilizers applied in world agriculture after the Second World War is one of the factors of global food security. At the same time, it is accompanied by an aggravation of environmental problems, both due to the increase in the overall load on agroecosystems and due to the imbalance between nutrients [1]. In particular, the ratio of N:P in the composition of mineral fertilizers increased from 2.4 in 1961 to 6.2 in 2013 [2]. The new paradigm of responsible sustainable fertilizer management includes nutrient roadmaps focused on sustainability, climate neutrality, nutrient recycling, digital solutions and accelerated innovation [3, 4].

In Ukraine, the aggression of the russian federation limits the ability of farmers to apply mineral fertilizers in the required amount, which prompts the search and implementation of ways to increase their efficiency. One of the directions of such improvement of fertilization systems is the optimization of the ratio of nutrients. This allows not only to increase the effectiveness of fertilizers, but also to improve the stress resistance of plants, because it is known that the mutual regulation of N and P cycles determines the response of organisms to climatic and atmospheric changes, forms the structure of food chains, microbiological activity and the release of nutrients from the soil [5, 6]. Conversely, unbalanced fertilization reduces the efficiency of plant consumption of nutrients from the soil and fertilizers, in particular, nitrogen fertilizers [7, 8].

The interaction between N and P can contribute to plant nutrition through the formation of branched root architecture [9, 10], an increase in the rate of colonization of arbuscular mycorrhizal fungi [11], and an increase in the active transport system for absorption of inorganic nitrogen and phosphorus [12]. The role of phytohormones, particularly strigolactones, in the formation of the early nitrogen-phosphorus signaling system has also been proven [13]. With a lack of moisture in the soil, plants reduce the absorption of nitrogen and phosphorus due to changes in the course of physiological processes, slowing down of the mineralization of soil organic matter and plant residues, and a decrease in diffusion in the soil [14-17]. Wetting the soil at the end of the drought enhances mineralization, which is accompanied by the release of nutrients from the dead microbial biomass that accumulated during the drying period [18]. It was established that with the increase in aridity of the climate, the cycle of nitrogen and phosphorus in the soil can be unbalanced due to a decrease in the concentration of the first element and an increase in the concentration of the second element, since the diffusion coefficient of P is more sensitive to soil moisture than the diffusion coefficient of N [19, 20].

At the same time, adjusting the N:P ratio in the soil by optimizing the doses and forms of mineral fertilizers, taking into account the level of moisture supply, allows for a purposeful influence on the yield of agricultural crops, as well as the concentration of nutrients in plants. According to Harpole W.S. with sang [21], Güsewell S. and Koerselman W. [22], Olde Venterink H. [23] and Palo F.D. with Fornara D.A. [24], changes in the N:P ratio in the soil may be more important than changes in the content of these elements. Most often, the deficiency of N and P is manifested in vegetative plants at $N/P<10$ and $N/P>20$, although these parameters also vary depending on the species, growth intensity, stage of development, etc. [25]. This makes it possible to develop tools for quantitative assessment of critical N:P ratios in individual crops [26] or gradations of N:P ratios in the soil, which would indicate limitations in the availability of nitrogen or phosphorus for plants, as is done for forest plantations of various types [27].Research in this direction is conducted in various countries and aims to balance the biogeochemical cycles of N and P in modern agroecosystems [28, 29]. It is expected that due to the selection of species with a higher optimal N:P ratio and a greater ability to consume phosphorus, the introduction of balanced crop rotations and fertilization systems, it is possible to optimize the stoichiometry of the ecosystem to achieve maximum plant productivity with the least risks to the environment [30, 31].

Goal. Determination of N:P ratios in soil, fertilizers and plants under different conditions of moisture supply for further development of climate-oriented crop fertilization systems.

Research materials and methods. The research was carried out at the soil and agrochemical scientific-research training ground on the territory of the SE "DG Grakivske" NSC "ISSAR named after O. Sokolovsky” (Kharkiv region, geographic coordinates: 49˚97′ N, 36˚01′ E), where the soil cover is dominated by chernozems and dark gray podzolized soils, but there are also contours of their eroded, elevated moistened and washed varieties [32]. The land plot with an area of 24 hectares was divided into 24 geo-positioned monitoring sites, where mixed soil samples were taken at a depth of 0-20 cm during 2018-2020 in two periods - in spring and autumn.

For experimental studies of the N:P ratio on the same site, two plots were chosen, which systematically differed in terms of moisture supply due to the peculiarities of the microrelief. The best moisture reserves are characteristic of site 1 with highly hydrated podzolized chernozems, located in a shallow depression, and somewhat worse – site 2 with modal podzolized chernozems. In each plot, a field experiment was laid according to the method described in detail in [33], namely: experimental plots in the shape of a circle with a diameter of 5 m were divided into four sectors with different ratios of N:(PK) – 1:1; 1:0.7; 1:0.5 and 1:0.3, which was created by applying 30, 60 and 120 kg/ha ac. s. nitrogen with fertilizers, respectively, on the general mineral background $N_{60}P_{60}K_{60}$ (Fig. 1).

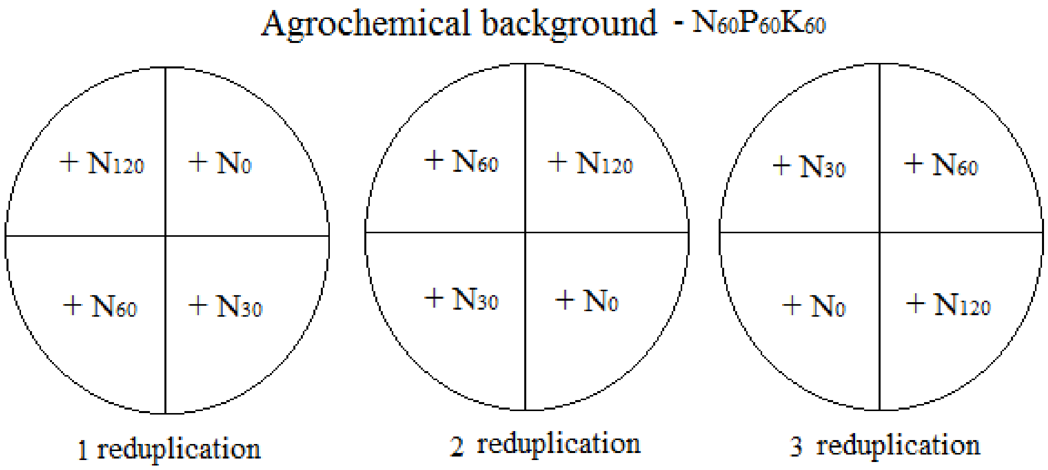


Fig. 1. Scheme of a field experiment to study the imbalance of nutrition of agricultural crops

The research was carried out during the growing season of 2021, the selection of soil samples was carried out before the start of the experiment and during the growing season of soybeans (phase of the third trifoliate leaf, ripening phase).

In order to identify patterns of changes in the N:P ratio in plant products in years with different hydrothermal conditions, a retrospective analysis of the stock data of the stationary field experiment "Effectiveness of mineral fertilizers depending on the level of nutrient availability" was carried out in 1969 on the same experimental field (certificate experiment No. 08). Detailed information about the scheme and methodology of conducting this experiment is given in [34].

In soil samples, the content of mobile forms of phosphorus and potassium was determined after extraction of 0.5 n CH_3COOH according to Chirikov's method according to DSTU 4115, nitrate nitrogen photometrically with disulfophenolic acid, ammonium nitrogen - photometrically with Nessler's reagent according to DSTU 4729. Soil moisture was determined by the thermostat-gravimetric method. The content of nitrogen, phosphorus and potassium in plant samples was determined after ashing with a mixture of sulfuric and perchloric acid according to the Ginzburg method. Statistical processing of the research results by the methods of dispersion and regression analysis was carried out using the STATISTICA 13.5.0.17 software.

Research results and their discussion. During the 2018-2021 research, periods with low precipitation (significantly below the long-term average) and normal or even increased moisture were clearly observed. In the driest year of 2018, the drying-wetting cycles were short-term and of equal duration. In 2019 and 2020, droughts were significantly longer than periods of normal moisture, but alternated with periods of abundant precipitation that exceeded the average multi-year amounts (Fig. 2).

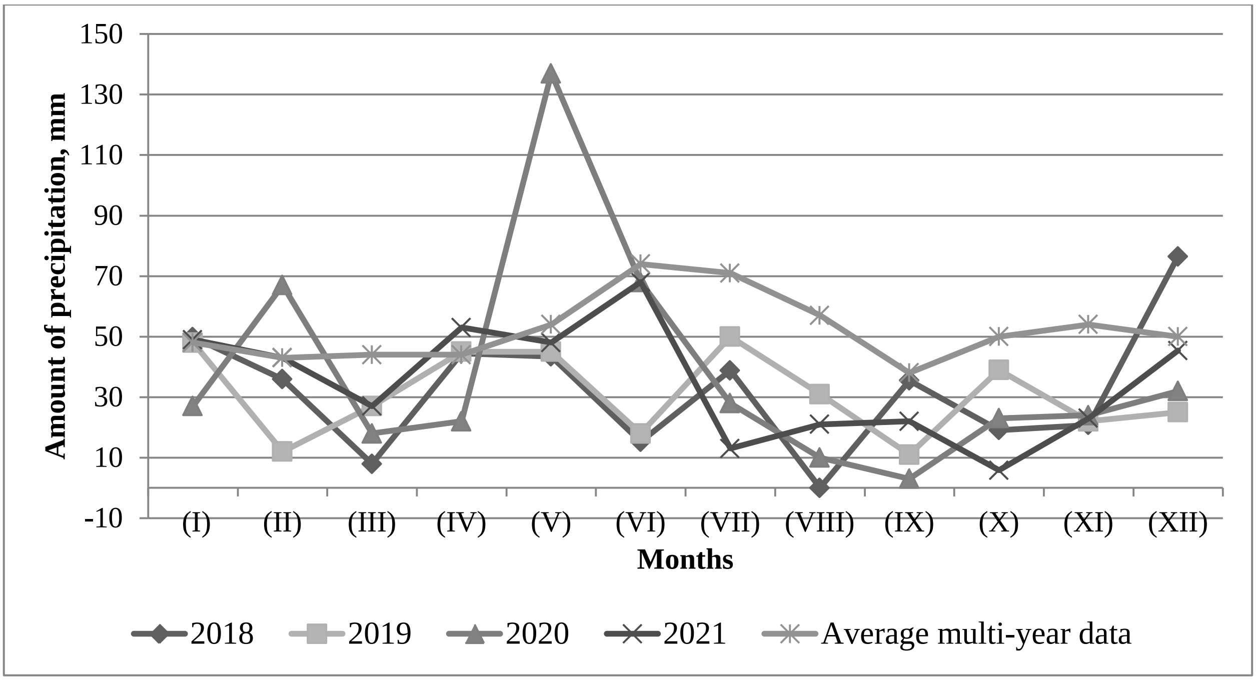


Fig. 2. The amount of precipitation in the years of research 2018-2021

Due to the fact that during rainy periods, nitrate forms of nitrogen easily migrate with the flow of moisture, and under favorable conditions for the mineralization of organic matter, their content in the arable layer increases rapidly, the variability of moisture has an effect on the dynamics of the N:P ratio in the soil. The coefficients of variation of the N:P ratio ranged from 35 to 103% in time and from 18 to 39% in space and were very similar to the coefficients of variation of mineral nitrogen (26-135% and 11-57%). On the other hand, the variability of the content of mobile phosphorus was smaller: 3-17% in time, 22-32% in space.

In the soil cover of the testing site, separate locations with a significantly higher N:P ratio in the arable layer due to an increase in the concentration of mineral nitrogen were found, the location of which mostly coincided with the areas of soil moisture accumulation (r=0.52-0.55). At the same time, at an unsatisfactory level of productive moisture reserves in the 0-20 cm soil layer, a decrease in its content by every 1% led to a decrease in the N:P ratio by 10%, and at a satisfactory level - by 4%. That is, the deterioration of the soil moisture supply was accompanied by a shift in the ratio of available forms of nutrients in the direction of increased nitrogen deficiency.

The revealed influence of spatial heterogeneity of soil moisture supply on the N:P ratio determines the feasibility of differentiating the fertilization of agricultural crops for soil areas 1 and 2, which differ in terms of moisture conditions. In particular, before sowing soybeans, the moisture reserves in the plowed soil layer of plot 1 was 19.9 mm, and plot 2 – 12.1 mm. At this time, with almost the same total content of mineral nitrogen in the soil at both sites, the ratio of nitrate and ammonium forms differed by two times (1:1 and 1:0.49, respectively), which is a consequence of inhibition of ammonification under drier conditions [35].

1. The content of mobile forms of nutrients in the arable layer of the soil at the beginning of the experiment

Experiment options	Nutrient content, mg per kg of soil				
	N mineral	$N\text{-}NO_3$	$N\text{-}NH_4$	P_2O_5	K_2O
Plot 1	5,14	2,55	2,59	69,9	83,6
Plot 2	5,99	4,02	1,97	74,4	84,3

Later, during the growing season of soybeans, the ratio of N:(PK) in the soil of both experimental plots narrowed due to the greater consumption of nitrogen compared to phosphorus and potassium and the high phosphate and potassium buffering of chernozems (Table 2). For experimental site 1 with better moisture conditions, the change in the N:(PK) ratio according to the experimental variants at the beginning and at the end of the soybean vegetation had a constant step (from 1.3 to 1.7), while each increase in the nitrogen dose by 30 kg/ha was accompanied by a significant increase in the content of mineral nitrogen in the soil (from 11.5 to 60.7 mg/kg). In experimental site 2 with lower moisture reserves, the ratio of N:(PK) at the beginning of the growing season was significantly wider than in site

1, and at the end of the growing season it was almost no different for nitrogen doses N_{60} and N_{90} and N_{120} and N_{180}.

2. N:P:K ratio in fertilizer mixture and soil

Experiment options	The ratio of N:P:K in the fertilizer mixture	The ratio of N:P:K in the soil at the beginning of the soybean growing season	The ratio of N:P:K in the soil at the end of the soybean growing season
Plot *1*			
$N_{60}P_{60}K_{60}$	1:1,0:1,0	1:6,5:7,5	1:14:17
$N_{90}P_{60}K_{60}$	1:0,7:0,7	1:4:5	1:9,5:10
$N_{120}P_{60}K_{60}$	1:0,5:0,5	1:2:2	1:6:6,5
$N_{180}P_{60}K_{60}$	1:0,3:0,3	1:1:1,5	1:4:4
Plot *2*			
$N_{60}P_{60}K_{60}$	1:1,0:1,0	1:11:12,5	1:9,5:9
$N_{90}P_{60}K_{60}$	1:0,7:0,7	1:5:6	1:10:9,5
$N_{120}P_{60}K_{60}$	1:0,5:0,5	1:3:3,5	1:6:6,5
$N_{180}P_{60}K_{60}$	1:0,3:0,3	1:2:2	1:6:5,5

Soybeans are very sensitive to the level of soil moisture, which during the growing season should not be lower than 70-80% of the lowest moisture content, so the dry weather conditions of 2021 with a severe drought in July had a negative effect on the yield (Table 3). The highest yield of soybeans (which is 40% higher than the control option) in the better-moistened plot 1 was recorded with fertilizer rates of $N_{180}P_{60}K_{60}$, and in plot 2 (which was 25% higher than the control option) – with $N_{120}P_{60}K_{60}$, and this confirms the inexpediency of increasing application nitrogen with insufficient moisture supply.

With an increase in the rate of nitrogen application from 60 to 180 kg/ha in plot 1, the content of this element in grain increased significantly, while the content of phosphorus decreased. In contrast, in the drier plot 2, the ratio of N:P in the grain was more stable (1:0.36-0.38) and corresponded to what occurred at the highest level of nitrogen application in plot 1 and is the closest to the normative values assimilation of nutrients by soybean plants (1:0.3:0.4 according to [36, 37]).

3. Soybean yield, the content of nutrients and their ratio in the grain for different ratios of N:(PK) in the composition of fertilizers

Experiment options	The ratio of N:P:K in the fertilizer mixture	Grain yield, t per ha	Content of nutrients in grain, %			$N:P_2O_5:K_2O$ ratio in grain
			N	P_2O_5	K_2O	
Plot *1*						
$N_{60}P_{60}K_{60}$	1:1,0:1,0	1,71	3,77	1,81	2,36	1:0,48:0,62
$N_{90}P_{60}K_{60}$	1:0,7:0,7	1,97	3,95	1,77	2,30	1:0,45:0,58
$N_{120}P_{60}K_{60}$	1:0,5:0,5	2,20	4,08	1,75	2,12	1:0,42:0,52
$N_{180}P_{60}K_{60}$	1:0,3:0,3	2,40	4,22	1,63	2,00	1:0,38:0,47
LSD($p \leq 0.05$)		*0,16*	*0,2*	*0,17*	*0,19*	-
Plot *2*						
$N_{60}P_{60}K_{60}$	1:1,0:1,0	1,92	4,11	1,59	2,19	1:0,38:0,53
$N_{90}P_{60}K_{60}$	1:0,7:0,7	1,92	4,19	1,51	2,12	1:0,36:0,50
$N_{120}P_{60}K_{60}$	1:0,5:0,5	2,40	4,35	1,60	2,15	1:0,37:0,49
$N_{180}P_{60}K_{60}$	1:0,3:0,3	2,19	4,31	1,60	2,01	1:0,37:0,46
LSD($p \leq 0.05$)		*0,17*	*0,1*	*0,05*	*0,1*	-
LSD*($p \leq 0.05$) *of the experiment		***0,20***	***0,4***	***0,25***	***0,21***	-

Similar observations of a narrowing of the N:P ratio in soybeans in colder regions of China with 400-500 mm May-September rainfall were made by Zhao et al. [38], who consider this a sign of excess phosphorus application under such hydrothermal vegetation conditions. The conditions of research at the SE "DG "Grakivske" are much drier, because the average amount of precipitation for May-September 2018-2021 was only 176 mm, during the entire period of the stationary field experiment - 264 mm with fluctuations from 164 mm to 435 mm. Despite this, a retrospective analysis of the data of this stationary experiment on the content of nutrients in plant products shows that for other grain crops (winter wheat, barley, pea-oats) the general regularity of the expansion of the N:P ratio in dry years is also inherent, and this is true both for the main (Fig. 3) and non-marketable part of the crop (Fig. 4). The statistical characteristics presented in these graphs also clearly show that the influence of hydrothermal conditions of growing agricultural plants on their chemical composition is much stronger than the effect of mineral fertilizers, due to which the N:P ratio can be adjusted within the confidence interval values.

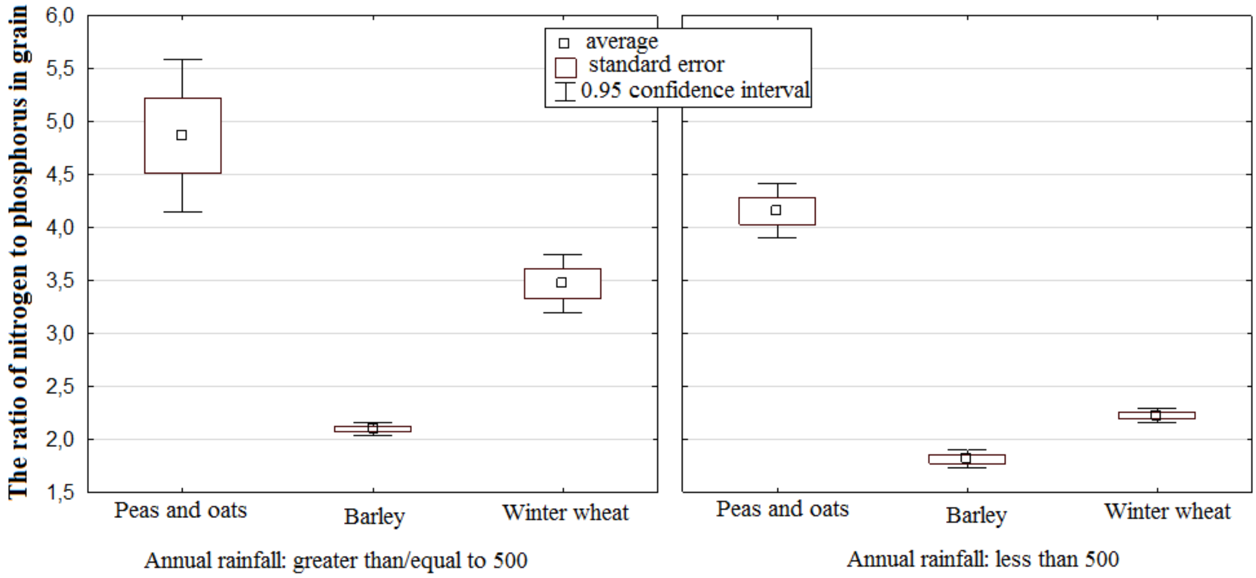
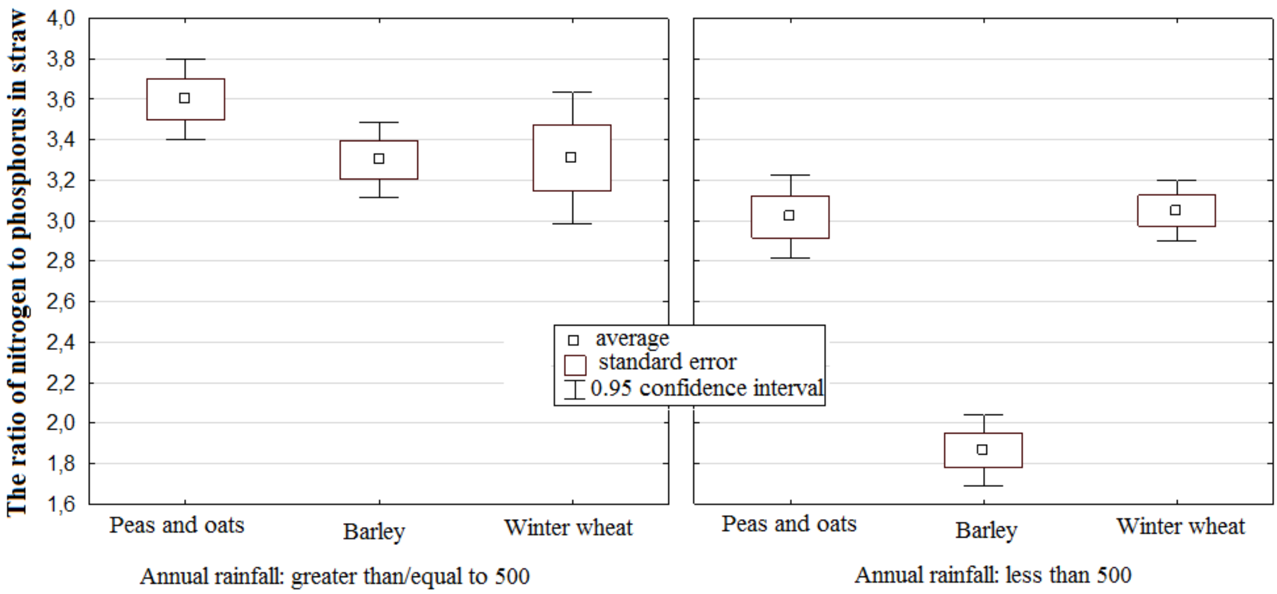


Fig. 3. N:P ratio in the main products of field crop rotation in years with different annual precipitation



Rice. 4. N:P ratio in non-commercial products of field crop rotation in years with different annual precipitation

Conclusions.

The ratio of nitrogen and phosphorus in the soil and plant products has spatial and temporal variability associated with the level of moisture supply, the use of fertilizers, the course of microbiological processes and the consumption of these elements by plants. The spatial component consists in a wider ratio of the forms of mineral nitrogen and mobile phosphorus available to plants in the arable layer of micro-lows inside the field, the temporal variability is expressed in a decrease in the wetter years of the N:P parameters in the main and by-products of field crop rotation, in particular winter wheat, barley, peas and oats Using the example of soybeans, it was established that under better moisture conditions, the optimal ratio of N:P in the composition of fertilizers changes in the direction of increasing the rate of nitrogen application per unit of phosphorus.

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