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ORIGINAL PAPER

DYNAMICS OF THE FORMS OF NUTRIENT NITROGEN IN GREYIC LUVIC PHAEOZEM WHEN REGULATING THEIR RESOURCES WITH FERTILIZERS AND NITRAPYRIN APPLIED TO WINTER BARLEY

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Abstract

This experiment was conducted at the Lviv National University of Nature Management (LNUP – Dublyany) in 2020-2021, in the Pasmovo Pobuzhye area of the Western Forest-Steppe of Ukraine, on soil that was dark-gray, podzolic light loam, low in humus (Greyic Luvic Phaeozem). The study aimed to determine the activity of nitrapyrin in the form of N-Lock™ in soil after applying different doses and forms of nitrogen fertilizers to a winter barley field. The agrochemical properties of the soil were determined according to classical indicators. The soil reaction in the 0-20 cm horizon was slightly acidic, with pH_{KCl} of 6.10-6.11. The content of easily hydrolyzable N in the 0-20 cm horizon was 65-70 mg kg^{-1} of soil, decreasing down to the depth 40 cm to 50-53 mg kg^{-1}. The content of nitrate anion changed from 20-28 mg kg^{-1} in the 0-20 cm layer to 16-18 mg kg^{-1} in the 20-40 cm layer. Fertilization of winter barley N37 in the phase of the onset of spring vegetative growth with the introduction of N23P60K60 in the autumn for pre-sowing cultivation without the use of nitrapyrin was less effective. The use of the urease inhibitor in the early vegetative growth phase rather than at the phase of resumed vegetative growth alongside the same doses of mineral fertilizer contributed to the harvest of 7.1 and 7.4 Mg ha^{-1} grain in 2020 and 2021, respectively. In general, the yield of winter barley correlated with the dose of nitrogen fertilization in 2020 (r ± = 0.76) and in 2021 (r ± = 0.81), while the concentration of nitrates in the arable layer correlated with the dose of fertilizer in 2020 (r ± = 0.88). The calculation of the payback of fertilizers showed that the application of N23P60K60 $(NH_4)_2HPO_4 + NH_4NO_3 + KCl$ + N37 (NH_4NO_3) + nitrapyrin (N-Lock™) in the phase of spring vegetative growth is the most economically viable option of providing nitrogen nutrition to winter barley in the market situation of 2021.

Keywords: nitrogen doses, nitrate, nitrapyrin, winter barley, grain yield

INTRODUCTION

Nitrogen (N) is a very important nutrient that contributes to the optimal growth and yield of all agricultural crops. With the increasing human population, the annual global demand for N chemical fertilizers is continuously increasing (Lassaletta et al. 2016). Global N containing fertilizer uptake in 2020 was 110 Mt (IFA, 2019) and continues to grow. The use of nitrogen from fertilizers is low and its losses are very high. Depending on the crop, agronomy practices and soil type, more than half of the supplemented N fertilizer can be lost to the environment (Yan et al. 2020). Nitrogen losses contribute to the eutrophication of water bodies (Ascott et al. 2017, Wang et al. 2019). Therefore, new solutions are sought to retain nitrogen in the soil and improve its fertilization efficiency, e.g. through the use of urease inhibitors.

The yield of winter barley largely depends on the quality of soil. A factor limiting the yield of barley most severely is the soil reaction. Nevertheless, barley is the fourth cereal in terms of yields (155 million tons) and cultivation area (66.6 million ha) – Noworolnik, Leszczyńska (2017).

In terms of grain yield, winter barley exceeds spring barley and spring wheat (Vlokh, Tuchapsky 2004, Shcatula, Barsky 2021). The distribution of this cereal in Ukraine is dictated by the country's natural conditions. Likewise, the supply of mineral fertilizers, in particular, nitrogen fertilizers, should also adjusted accordingly. Nitrogen stimulates growth processes from tillering, increases the respiration rate and metabolic rate, but at the same time excessive nitrogen nutrition and adverse weather events raise a higher risk of lodging (Klymyshyna 2011). The maximum use of nitrogen by winter barley occurs in the period from the tillering phase (BBCH 22) to the end of the phase of stem elongation (BBCH 30).

A four-field, crop rotation, mineral fertilization system with the introduction of N128 annually on average increased the content of easily hydrolyzable nitrogen in Greyic Luvic Phaeozem of the Western Forest-Steppe of Ukraine from 99 to 111 Mg kg^{-1} of soil in eight years (Poliovyy et al. 2021). Nitrogen use efficiency by plants and agronomic efficiency values were dependent on the fertilization variants and nitrogen doses (Szulc et al. 2019).

The nitrogen resources available to winter barley in the soil can be most easily regulated by manipulating autumn and spring fertilization regimes with ammonium nitrate or urea (Qin et al. 2010). In experiments with ammonia and nitrate nutrition of winter barley, the same efficiency was confirmed. However, nitrification, the process of oxidation of ammonium nitrogen to nitrate, causes the conversion of ammoniac forms of nitrogen into water-soluble one, nitrate, which can be lost in vertical soil run-offs (Singh, Verma 2007, Shibata et al. 2015, Torma et al. 2019, Fu et al. 2020, Hes et al. 2020). Groups of nitrifiers are bacteria of the species *Nitrosomonas*, *Nitrosocystis*, *Nitrosolobus*, *Nitrobacter*, *Nitrococcus* (Gubry-Rangin et al. 2010, Beeckman et al. 2018, Li et al. 2018). Urea is the most popular nitrogen fertilizer. Urea is hydrolyzed through the catalysis of the microbial enzyme urease (Martins et al. 2017). Urease activity depends on the type of biogeocenosis and varies in the seasons of the year; for example, it increased rapidly in spring and autumn (111-327%), while in summer the enzyme activity naturally decreased twice in Prysamarya in the Eastern Forest-Steppe beyond the Dnieper (Kulyk et al. 2007, Zaman et al. 2009, Abalos et al. 2014). Urea nitrogen can be lost to form N_2O, N_2 or oxidized to nitrates by microbial nitrifiers (Zaman et al. 2009, Pärn et al. 2018, Fu et al. 2020).

Various chemical compounds have been evaluated for their effectiveness in reducing ammonia losses from urea by inhibiting urea hydrolysis (Takai, Horikoshi 2000, Ferguson et al. 2003, Rose et al. 2018, Byrne et al. 2020, The European Chemicals Agency 2020, Vilček et al. 2020, Anonymus 2021). Therefore, there is a variety of urease inhibitors. Thiophosphoric triamide (Sigurdarson et al. 2018) acts on urea for 7-10 days (Zaman et al. 2008). Dicyandiamide is a nitrification inhibitor that slows the oxidation of ammonia to nitrate by inactivating bacterial monooxygenase (Amberger 1986). Nitrapyrin is a chlorinated pyridine compound with the formula $ClC_5H_3NCCl_3$. Nitrapyrin is a widely used nitrification inhibitor in soils in the EU and the US (Zacherl, Amberger 1990, Dow Chemical 2012). 2-chloro-6- (trichloromethyl) pyridine, nitrapyrin, is a soil bactericide, acts as an inhibitor of the formation of urease, thus preventing the hydrolysis of urea. Its effect on soil bacteriocenosis and nitrification inhibition lasts for 8-10 weeks. Nitrapyrin decomposes in both soil and plants (Espín, García-Fernández 2014). Nitrapyrin is available as N-Serve™, Instinct™, N-Lock™, which have been marketed since 1974.

Nitrapyrin delays the nitrification process. It suppresses the bacteria *Nitrosomonas* spp., which converts ammonia to nitrite. Nitrapyrin thus retains more of the nitrogen applied with fertilizers in a form readily available to crops (Zacherl, Amberger 1990). This prevents the loss of soil nitrogen through leaching of nitrates (NO_3^-), or due to the emission of nitrogen gas (N_2) and nitrous oxide (N_2O) into the atmosphere (Zaman et al. 2008, Roche et al. 2016, Martins et al. 2017, Tian et al. 2017, Zhang et al. 2018). Nitrapyrin has been used in the United States and studied in various countries for over 40 years as a nitrification inhibitor to increase crop yields and reduce the environmental impact of nitrogen fertilizers used in agriculture (Anonymus, 2021).

Ukraine has undertaken the implementation of the Council of Europe Directive 91/676/EEC of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources (Nitrates Directive). It stipulates a number of documents that should guide the sectors of the economy. In particular, they are “Methods for identifying areas vulnerable to pollution by nitrate compounds” and “Code of Best Agricultural Practice” (Implementation 2020, 2020).

In Ukraine, in particular in the Western Forest-Steppe, the use of urease inhibitors is rare, and imports of nitrapyrin are unstable. However, the problem of obtaining high yields of winter barley with the maximum background of nitrogen nutrition and without nitrogen loss exists there.

Our study aimed to determine the effect of nitrapyrin in the form of N-Lock™ in Greyic Luvic Phaeozem by applying different doses and forms of nitrogen fertilizers for winter barley.

MATERIALS AND METHODS

The experiment was conducted at the Lviv National University of Nature Management (LNUP – Dublyany) in 2020-2021. The university has a research field on the Pasmove Pobuzza in the Western Forest-Steppe of Ukraine. The geographic coordinates are N 49°54′14″; E 24°05′10″, and the altitude above sea level is 258 m (Physical and geographical zoning ..., 2022; Anonymus, 2022a).

The technology of growing winter barley was traditional: plowing to 20-22 cm, fertilization with diamophos $(NH_4)_2HPO_4 + NH_4NO_3 + KCl$ – N10P26K26) for pre-sowing cultivation according to the experimental scheme (Table 1). The total doses of P and K were, respectively, 60 kg ha^{-1} in variants 2-12, as the background. Sowing was carried out with the chosen variety of barley, on optimal dates, with the recommended sowing rate of 3.8 million grains per hectare. Phases of ontogenesis of winter barley were recorded according to standard methods (Meier 2018).

Table 1

Scheme of the experiment

Variant code	Fertilizer components
1.	no fertilizers
2.	N23P60K60 $(NH_4)_2HPO_4$+NH_4NO_3+KCl) (before sowing)
3.	Nitrapyrin (before sowing)
4.	N97(CH_4N_2O) (before sowing)
5.	N97(CH_4N_2O) (before sowing) + nitrapyrin (before sowing)
6.	N97(CH_4N_2O) (before sowing) + nitrapyrin (in BBCH 21)
7.	N37(NH_4NO_3) (in BBCH 21)
8.	N37(NH_4NO_3) + nitrapyrin (in BBCH 21)
9.	N67(NH_4NO_3) (in BBCH 21)
10.	N67(NH_4NO_3) + nitrapyrin (in BBCH 21)
11.	N97(NH_4NO_3) (in BBCH 21)
12.	N97(NH_4NO_3) (in BBCH 21) + nitrapyrin (before sowing)

In the experiment, urea (CH_4N_2O – N46) was applied pre-sowing in the standard dose. Part of the nitrogen fertilizers in the form of ammonium nitrate (NH_4NO_3 – N34) was applied in the spring during the resumed vegetative growth, part – before earring (according to the experimental scheme). Nitrogen stabilizer (nitrapyrin, Dow Chemical 2012, N-Lock™), was applied in a dose of 1.2 dm ha^{-1} according to the experimental scheme.

Weed control was performed with the herbicide Triburon-methyl (25 g ha^{-1}). The grain was treated against diseases with Kinto Duo (2.0 dm^3 Mg^{-1}) and Sistiva fungicide (0.8 dm^3 Mg^{-1}) before sowing. Terpal (1.0 dm^3 ha^{-1}) was applied in a tank mix with Abacus (1.5 dm^3 ha^{-1}) and microelements in the VVSN 3 dm^3 phase with the growth regulator Chlormequat (1.2 dm^3 ha^{-1}).

The size of a plot is 37 m^2, and the area for harvest was 25 m^2. The field experiment was conducted in three replications.

The weather conditions were better in the autumn of 2020 than in the autumn of 2019. Therefore, the conditions for the formation of the winter barley harvest were better in the spring of 2021, despite the colder weather at that time.

The agrochemical properties of the soil were determined by classical indicators (Klute 1987). The analyses were performed in the laboratory of the branch of the Department of Agrochemistry and Soil Science of LNUP, which is affiliated with the Institute of Agriculture of the Western Region of the National Academy of Sciences of Ukraine.

Soil samples were taken and prepared for analysis in accordance to DSTU ISO 11464-2001. Determination of pH_{KCl} was performed by the potentiometric method according to DSTU ISO 10390: 2001 at a soil to solution ratio of 1: 2.5 in a salt extract of 1 mol dm^{-3} KCl solution. The nitrate nitrogen content (Nn) was determined potentiometrically using an ion-selective nitrate electrode in a salt extract of 1% solution of potassium alum at a 1: 2.5 soil to solution ratio. The content of nitrate nitrogen was determined from readings of an ionometer and the calibration graph. Standard solutions for calibration of the device and calibration graph were prepared using 1 10^{-1}M KNO_3 by gradually diluting it ten times with distilled water to a concentration of 1 10^{-2} M, 1 10^{-3} M, 1 10^{-4} M. Determination of easy hydrolysable nitrogen (Nh) was performed by the Cornfield method according to DSTU 7863: 2015. To this purpose, a batch of the soil was hydrolyzed with 1 mol dm^3 NaOH solution in Conway cups for 48 h in a thermostat at 28°C. As a result, nitrogen of organic compounds in the form of NH_3 was released, which was absorbed by the boric acid solution and then quantified by titration with 0.02 mol dm^{-3} H_2SO_4 solution.

The genetic and morphological structure of the soil had been described before the establishment of the experiment in a soil profile in the experimental field of the Lviv National University of Nature Management. Soil samples for laboratory analysis were also taken. The experimental plot lies in the lower declivous part of a slope. The experimental plot is arable land.

The surface of the soil is lumpy. The soil is dark-gray, podzolic light loam, low in humus (Anonymus 2022*b*), i.e. Greyic Luvic Phaeozem, 1961 (WRB 2015)

The content of clay in the top horizon was 28.4%, thus the soil has the granulometric composition of light loam. The content of clay increases with the depth of the soil horizon.

The content of humus in arable horizon was 2.18-2.38%, thus the soil is low in humus.

The reaction in the 0-20 cm horizon is slightly acidic, pH_{KCl} 6.10-6.11, and becomes more acidic, pH_{KCl} 5.97-6.01 to the depth of 40 cm. Hydrolytic acidity in the arable horizon is low, 2.40-2.80 cmol kg^{-1}. The total of exchangeable bases is 22.0-22.7 cmol kg^{-1}, which corresponds to a high level. The content of easily hydrolyzable nitrogen (N_h) in the 0-20 cm soil layer is 65-70 mg kg^{-1} of soil and decreases to 50-53 mg kg^{-1} to the depth 40 cm. The amount of available phosphorous (P) in the 0-20 cm layer is 49-50 mg kg^{-1}. Its content decreases gradually to 43-45 mg kg^{-1} with the depth. The content of available potassium (K) in the 20-cm layer is 34-36 mg kg^{-1}. Its content decreases to 25-28 mg kg^{-1} in the 20-40 cm layer. The weak mobility of available forms of nutrients was probably caused by the very high capacity of the sorption complex that appears in the Ukrainian soils.

Statistical reliability of indicators was calculated using MS Excel, Statistica 12 (by ANOVA method) (Anonymus, 2022*c*).

RESULTS

The lack of soil fertilization caused a low (natural) content of easily hydrolyzable nitrogen in the arable and subsoil horizons, and it decreased before harvest to 44-65 mg kg^{-1} dry weight (Figure 1 - var. 1). Application of N120P60K60 (N23 before sowing and N97 at the onset of spring vegetative growth in the form of urea – var. 4) resulted in an increase in the concentration of easily hydrolyzable nitrogen by 31-37 mg kg^{-1} in the 0-20 cm layer in both years of research. The application of nitrapyrin in object no. 5 (Table 1) contributed to an additional increase in the supply of easily hydrolyzable nitrogen by 8 mg kg^{-1} each year. Nitrapyrin was more effective when applied at the start of the spring growing season of winter barley (object no. 6) compared with its application under pre-sowing cultivation. An increase in the resource of easily hydrolyzable nitrogen at the beginning of the growing season was observed when N23P60K60 was applied in autumn + N37 at the start of spring vegetative growth (object no. 7). The application of nitrapyrin and the increase in the dose of N37 (object no. 8) and N67 (object no. 9) at the beginning of spring vegetation further increased the concentration of easily hydrolyzable nitrogen in the arable layer. Howe-

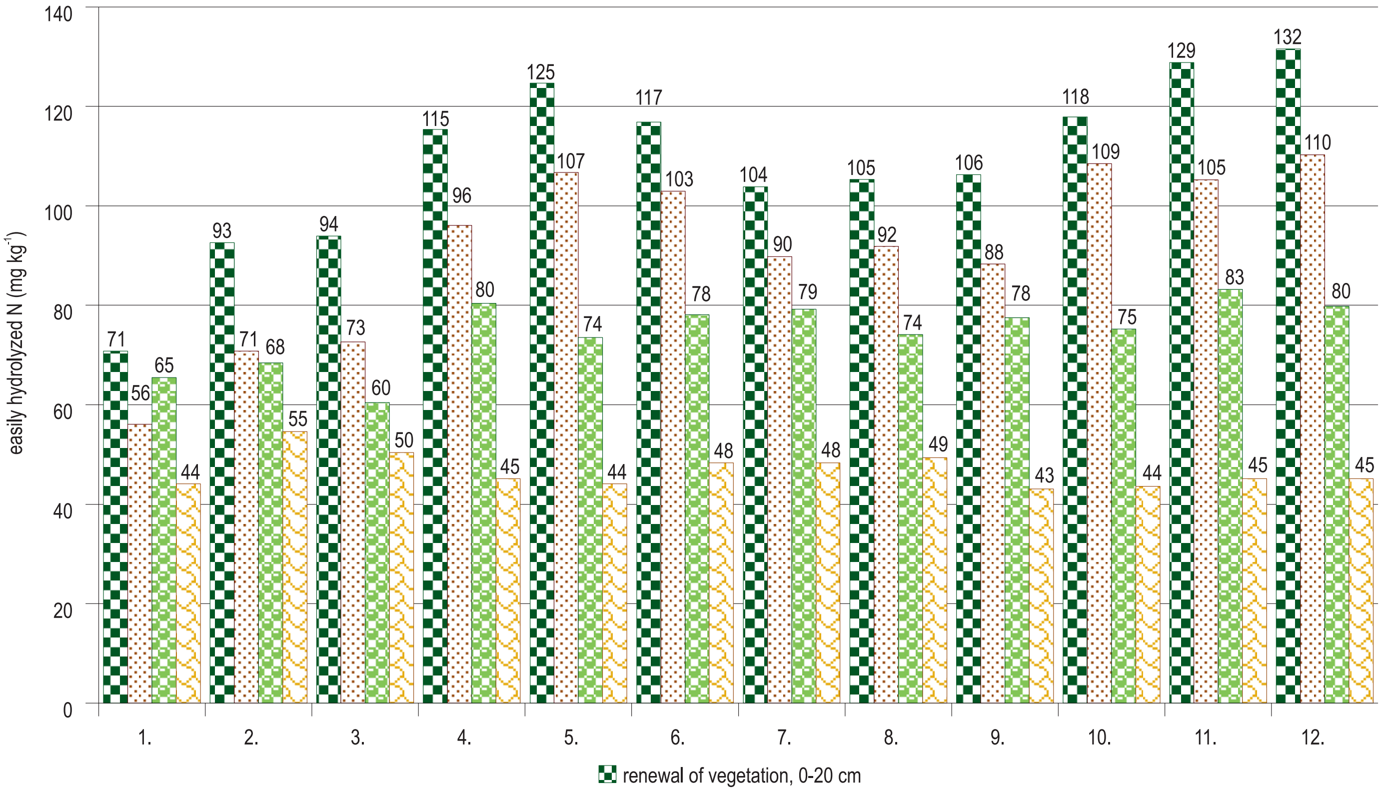

Fig. 1. Changes in easily hydrolyzable N resources in the soil under the influence of nitrogen fertilizer and nitrapyrin in the growing season of 2020. Experiment options – see Table 1

ver, its content peaked at 128-135 mg kg^{-1}, from using N23P60K60 in autumn + N97 at the start of spring vegetation without nitrapyrin (object no. 11) and with nitrapyrin (object no. 12) in both years of the study.

Nitrapyrin helped to increase the content of easily hydrolyzable nitrogen in the soil both when applied before sowing (3 mg kg^{-1} in autumn) and at the start of spring vegetative growth (6 mg kg^{-1} in spring) in both experimental years. In all variants, the combination of a nitrogen dose with nitrapyrin caused a relative increase in the resource of easily hydrolyzable nitrogen in arable and subsoil layers.

Nitrogen fertilizers increased the nitrate nitrogen concentration 2-4 times in the soil at the start of spring vegetative growth. For example, application of N23 before sowing + N97 urea (Figure 2 - object no. 4) or ammonium nitrate at the start of spring vegetative growth (object no. 11) led to an increase in nitrate nitrogen to 93-99 mg kg^{-1} of soil in 2020. Nitrapyrin, when applied at different times, significantly reduced the concentration of nitrates in arable and subsoil layers. However, nitrapyrin was more effective when applied making at the resumed growth of winter barley. However, in order to determine the effectiveness of nitrapyrin depending on different dates of application of nitrapyrin and fertilizers, longer studies are needed, covering different weather conditions of the growing season.

To determine the effect of fertilizers and nitrapyrin on soil acidity, we investigated the increase in the acidity of arable and subsoil layers under the influence of mineral fertilizers in 2020-2021. The alkalizing effect of nitrapyrin on the soil solution was established. However, alkalization of the soil with nitrapyrin was weakened by increasing the nitrogen dose from 23 kg ha^{-1} (Figure 3 - object no. 2) to 120 kg ha^{-1} (object no. 3, 4, 5 and others). The soil was acidified the most at N120 nitrate without nitrapyrin. By the time the winter barley was harvested, the soil was less acidic than it had been in the spring.

We harvested from 4.4 to 7.4 Mg ha^{-1} grain in 2020-2021 (Figure 4). The minimum yield was harvested from the soil with its natural fertility. Application of N97 (resumed vegetative growth) + nitrapyrin (pre-sowing cultivation) against the background of N23P60K60 (object no. 10 and 11) resulted in a maximum yield of 7.4 Mg ha^{-1} in 2021 and 7.3 Mg ha^{-1} grain in 2020 (object no. 11). The lower dose of N67 against the background of N23P60K60 when using nitrapyrin in the resumed vegetative growth (object no. 10) gave a lower yield of 7.4 and 7.3 Mg ha^{-1} grain in 2021 and 2020.

Fertilization of winter barley N37 in the phase of vegetation restoration against the background of N23P60K60 from autumn without the using nitrapyrin (object no. 7) provided a grain yield of 6.8-6.7 Mg ha^{-1} in 2020-2021. The introduction of urease inhibitor in the phase of vegetation restoration against this background of nitrogen-phosphorus-potassium fertilizer (object no. 8) contributed to the collection of 6.9 and 6.6 Mg ha^{-1} grain in 2020 and 2021.

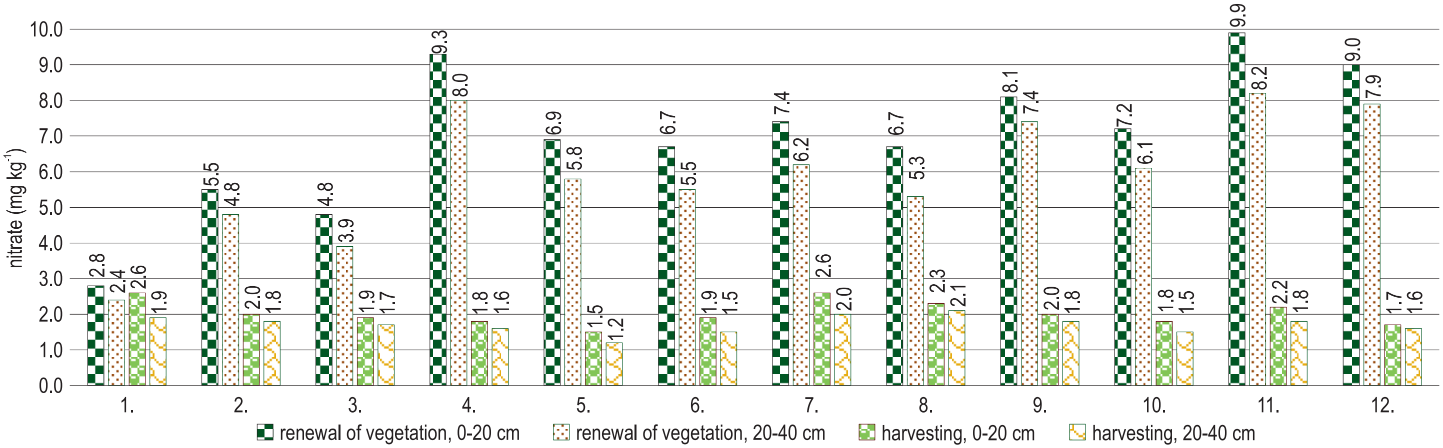

Fig. 2. Changes in nitrate resources in the soil under the influence of nitrogen fertilizer and nitrapyrin during the spring-summer vegetation in 2020 (all analytical parameters were within 0.05 level of statistical accuracy). Experiment options – see Table 1

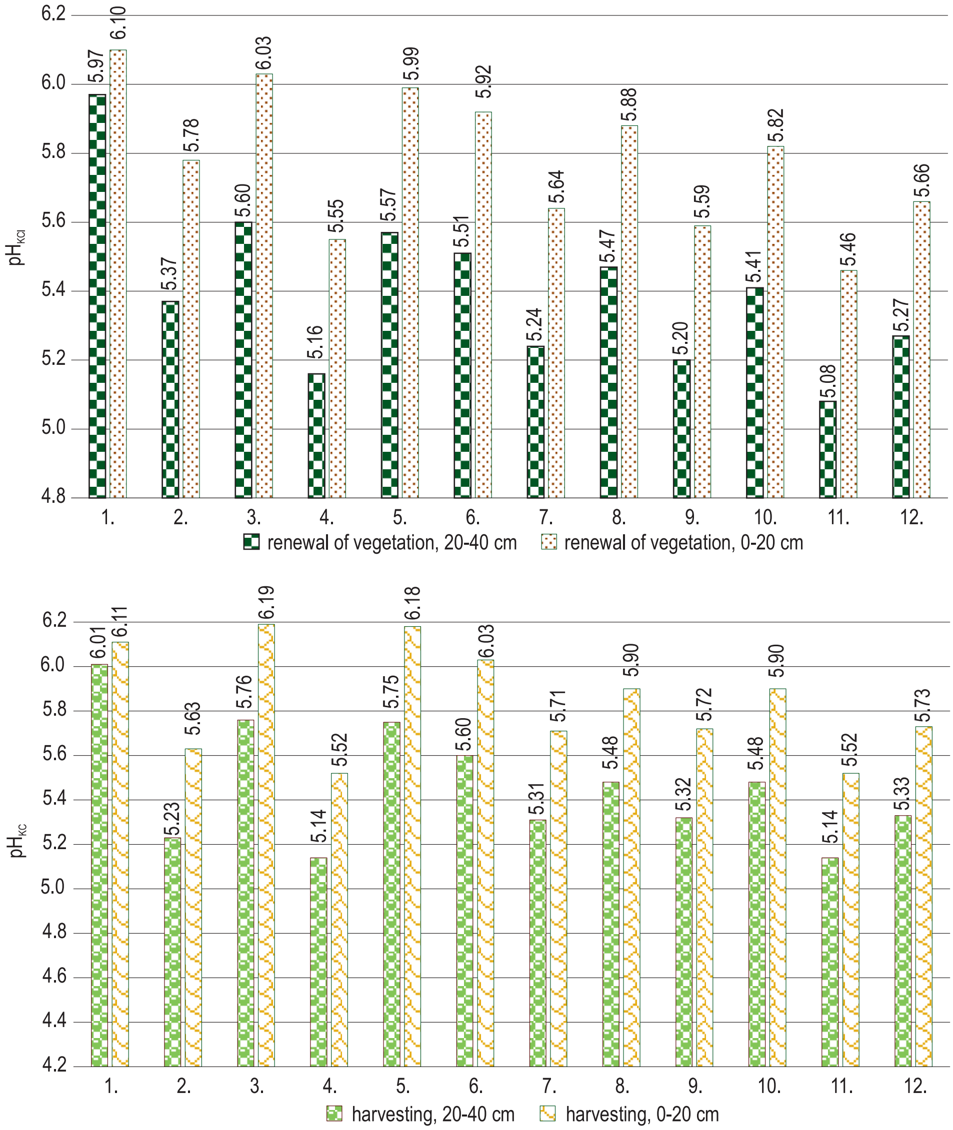

Fig. 3. Changes in soil pH_{KCl} under the influence of nitrogen fertilizer and nitrapyrin during the spring-summer growing season in 2020 (all analytical parameters were within 0.05 level of statistical accuracy). Experiment options – see Table 1

DISCUSSION

Our results were similar to the effects of applying nitrogen fertilizers to winter barley reported by some other researchers (Klymyshyna 2012, Roche et al. 2016). At the same time, the effectiveness of nitrapyrin

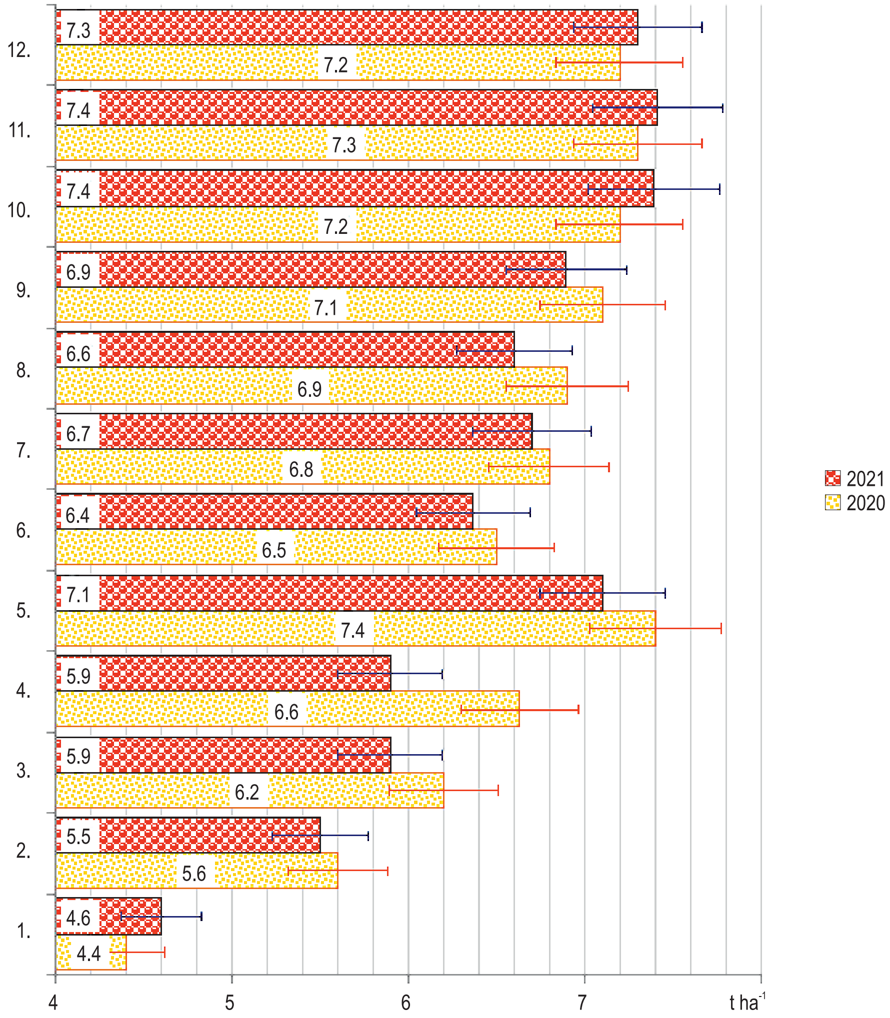

Fig. 4. Yield of winter barley depending on the dose of nitrogen and nitrapyrin in 2020 (all parameters were within 0.05 level of statistical accuracy – the error difference of average Sd = 1.30 Mg ha^{-1} for 2020 and 1,64 Mg ha^{-1} for 2021, the smallest absolute significant difference (05) = 2.63 Mg ha^{-1} for 2020 and 3.32 Mg ha^{-1} for 2021). Experiment options – see Table 1

in autumn or spring is still controversial (Amberger 1986, Abalos et al. 2014, Beeckman et al. 2018). It is different depending on natural areas of the world (Ferguson et al. 2003, Fu et al. 2020), on the use of different agricultural treatments (Qin et al. 2010, Babulicová, Dyulgerova 2018) and on different crop cultures (Martin et al. 1993, Abalos et al. 2014, Roche et al. 2016, Martins et al. 2017, Zhang et al. 2018).

The first goal of using urease inhibitors is to avoid excessive nitrate accumulation in the soil after applying nitrogen fertilizers. The second goal is to achieve the maximum crop productivity and fertilizer efficiency. We obtained the greatest effect from using N120 in the form of urea and ammonium nitrate in combination with nitrapyrin in the autumn and spring of 2020-2021 on average. The nitrification inhibitor provided 7.4 Mg ha^{-1} grains of winter barley, which is 0.8 tons more than achieved with urea alone. We obtained the same result from the division into N23 in autumn + N67 in spring and the use of nitrapyrin at the start of spring vegetation according to the 2020-2021 average.

The nitrification inhibitor nitrapyrin helped increase grain yield by 0.3-0.6 Mg ha^{-1} in combination with various fertilizer doses applied to for winter barley. The effect of nitrapyrin was manifested in expanding the content of easily hydrolyzable N and reducing the nitrate concentration at all nitrogen fertilizers doses. Thus, when applying 97 kg of ha^{-1} urea alongside N23, P60 kg of superphosphate and K60 kg of ha^{-1} potassium salt in autumn, the addition of nitrapyrin for pre-sowing cultivation reduced the nitrate content by 24 mg kg^{-1} of soil, while adding it to restore vegetation reduced it by 26 mg kg^{-1} soil while its content without the inhibitor was 93 mg kg^{-1} soil. At the same time, its use significantly alkalized the acid reaction of the soil at the beginning and end of the barley's growing season.

The grain yield of winter barley was very closely correlated (Table 2) with the concentration of easily hydrolyzable nitrogen and nitrate in the topsoil ($r = 0.85$) and subsoil ($r = 0.86$) layers in 2020. An inversely proportional correlation between yield and soil pH$_{KCl}$ was detected. The higher the yield, the less nitrate remained in the soil before the maturing of winter barley ($r = – 0.40$ in the upper stratum, $r = – 0.54$ in the subterranean stratum). In general, the yield of winter barley correlated with the dose of nitrogen in 2020 ($r = 0.76$) and in 2021 ($r = 0.81$), while the concentration of nitrates in the arable layer correlated with the dose of nitrogen in 2020 ($r = 0.88$).

The planar 3D model in Figure 5*a* demonstrates a positive synergistic effect of increasing the concentration of easily hydrolyzable N and nitrate N in the soil on the yield of winter barley grain. Therefore, the inhibition

Table 2

Relationship of winter barley grain yield with the content of easily hydrolyzable nitrogen and nitrate nitrogen in the soil and the dynamics of pH$_{KCl}$. r (±)

Nutrition factor of plant (2020)					
N_h		pH$_{KCl}$		N_n	
Depth of soil sampling (cm)					
0-20	20-40	0-20	20-40	0-20	20-40
Time of soil sampling – spring (after application of fertilizers and nitrapyrin)					
0.87	**0.89**	**-0.60**	**-0.69**	**0.88**	**0.86**
Time of soil sampling – on harvest					
0.17	0.31	-0.42	**-0.54**	-0.44	-0.39

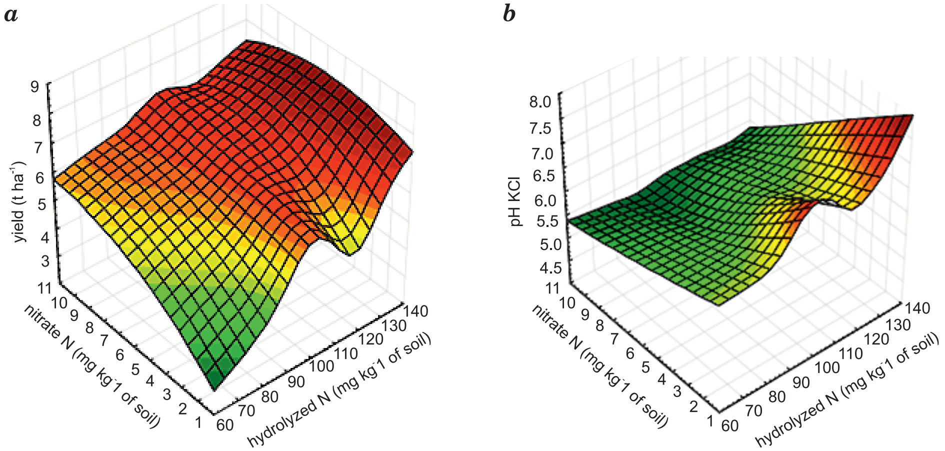

Fig. 5. Planar 3D model of the influence of the ratio of different forms of nitrogen in the soil and nitrogen doses on the yield of winter barley and the change of pH_{KCl} of the soil according to the data obtained in the experiment (for the given indicators weighted least squares)

of urease activity by nitrapyrin did not negatively affect the nutrition of winter barley with nitrogen substances from the soil to obtain the maximum yield.

The planar 3D model in Figure 5*b* shows a distinct tendency of soil acidification with an increasing nitrate concentration. An increase in the concentration of hydrolyzed N moderately neutralizes soil acidity at low levels of the nitrate N content. Therefore, the action of nitrapyrin restrained soil acidification by nitrogen fertilizers owing to the inhibition of urease activity, which ensures the rapid formation of excess nitrate N.

Many authors (Singh, Verma 2007, Zaman et al. 2008, Hess et al. 2020) argued that urease inhibition reduced leaching, neutralized soil acidity (Fu et al. 2020), and also restrained the emission of gaseous forms of nitrogen into the atmosphere (Martins et al. 2017; Tian et al. 2017, Byrne et al. 2020). Although we did not study some of these phenomena, we assume that our optimal dose of nitrogen fertilizers in combination with nitrapyrin also caused these positive effects.

The economic result of growing winter barley grain showed that the highest net profit could be obtained with the fertilization regime: N23P60K60 $(NH_4)_2HPO_4$+NH_4NO_3+KCl) (before sowing) + N37(NH_4NO_3) (during the resumed vegetative growth) (object no. 7) – 896.73 \$ h^{-1} (Figure 6).

High levels of profitability were calculated at higher application doses of nitrogen fertilizers and nitrapyrin. However, the return on costs for fertilizers and nitrapyrin decreased from 2.57 \$/\$ per object no. 8 to 1.42 \$/\$ per object no. 12 of the experiment.

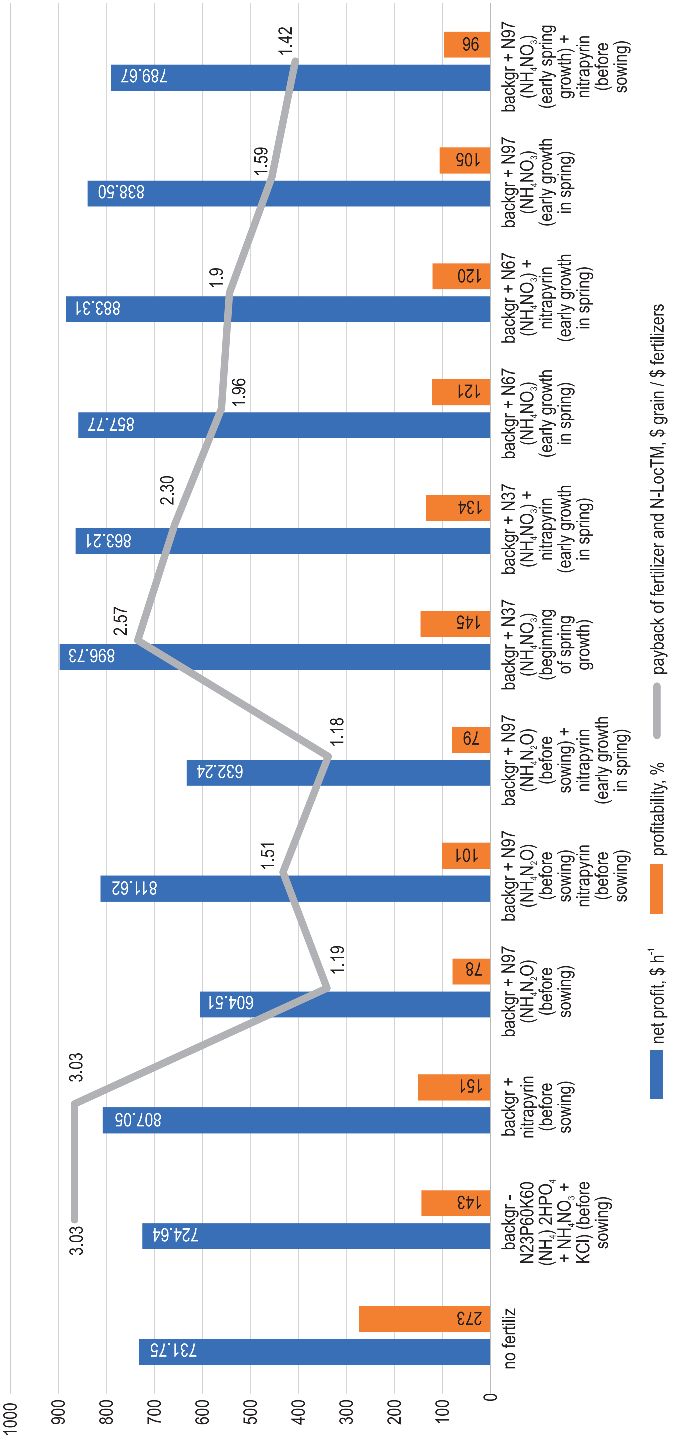

Fig. 6. Payback of using fertilizers and N-Lock™ in growing winter barley (at the rate: 30 - for one $ and 256 $ for one ton of grain)

CONCLUSIONS

Applying the maximum amount of nitrogen fertilizers under winter barley in different forms of fertilizers (N97P60K60) and at different times resulted in the maximum increase in the concentration of easily hydrolyzable nitrogen and nitrates in the arable (0-20 cm) (117-132 mg kg^{-1}) and subsoil (20-40 cm) (103-110 mg kg^{-1}) layers of Greyic Luvic Phaeozem. However, this did not ensure the highest level of grain harvest of winter barley of the Highlight variety. Nitrapyrin caused an increase in the content of easily hydrolyzable nitrogen by inhibiting the formation of nitrates when applied in the fall before sowing, and in the spring when the vegetative growth resumed. Increasing the dose of nitrogen fertilizer acidified the entire soil, while the action of nitrapyrin contributed to its alkalization. The concentration of easily hydrolyzable nitrogen and nitrate nitrogen was closely positively correlated (respectively $r \pm = 0.87$-0.89 and 0.88-0.86) with the grain yield, and soil acidity was negatively correlated with the yield ($r \pm = -0{,}42$ and 0.54).

Fertilization of winter barley N23P60K60 $(NH_4)_2HPO_4+NH_4NO_3+KCl$) + N97($CH_4N_2O$) and use of nitrapyrin (before sowing) were effective. The grain yield was by 0.8 t ha^{-1} in 2020 and 1.2 Mg ha^{-1} in 2021 higher than without nitrapyrin.

Fertilization of winter barley N23P60K60 ($(NH_4)_2HPO_4+NH_4NO_3+KCl$) + N97($NH_4NO_3$) and use of nitrapyrin at the phase of resumed vegetative growth (BBCH 21) ensured a yield of 7.2 t ha^{-1} in 2020 and 7.4 t ha^{-1} in 2021. The use of nitrapyrin replaced an additional dose of N30 nitrogen fertilizers. The yield of winter barley was proportionally correlated with the dose of nitrogen fertilizer in 2020 ($r \pm = 0.76$) and in 2021 ($r \pm = 0.81$), and the concentration of nitrates in the arable layer was correlated with the dose of fertilizer application in 2020 ($r \pm = 0.88$).

The calculation of the payback of fertilizers in the form of $(NH_4)_2HPO_4$ + NH_4NO_3 + KCl and CH_4N_2O (before sowing according to N120P60K60) and also nitrapyrin in the form of N-Lock™ and the application of N23P60K60 (NH_4) 2HPO$_4$ + NH_4NO_3 + KCl before sowing + N67 (NH_4NO_3) + nitrapyrin (N-Lock™) in the resumed vegetative growth phase (BBCH 21) are cost-effective options for providing nitrogen nutrition to winter barley in the market situation in 2021.

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