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VARIA

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ECOLOGICAL CHEMISTRY AND ENGINEERING A

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LONG-TIME EFFECT OF HARD COAL FLY ASHES APPLICATION ON NITROGEN CONTENT IN THE SOIL

NASTĘPCZE ODDZIAŁYWANIE POPIOŁÓW Z WĘGLA KAMIENNEGO NA ZAWARTOŚĆ AZOTU W GLEBIE

Abstract: The paper discusses the long-term effect of hard coal fly ashes on the content of some nitrogen forms in soil. The study was based on a field experiment 19 years after it had been established. Fly ashes were dosed at rates of 0, 100, 200, 400, 600 and 800 Mg ha^{-1}, in the following four series: without organic substance, with farmyard manure, with straw and with tree bark. The results seem to prove that hard coal fly ashes as well as organic fertilizers applied in addition to fly ashes had a significant influence on the long-term content of the analyzed forms of nitrogen in soil. The effect of fly ashes was particularly evident in the arable horizon of the analyzed soil. In deeper soil layers, fly ashes were found to have no influence on the content of the analyzed nitrogen forms. Among the organic amendments tested in the experiment, irrespective of the depth at which soil samples were taken, tree bark had the strongest influence on N-NO_3, increasing its content. With respect to N-NH_4, the strongest influence on its content was produced by straw.

Keywords: hard coal fly ashes, nitrogen, ammonia nitrogen, nitrates

The regulations introduced to the Polish law over the last few years, regarding air pollution control, have resulted in considerably depressed emission of fly ashes from energy generating facilities. In 1990, about 1,430 thousand tonnes of fly ashes were emitted into the atmosphere, and that amount was reduced to about 112 thousand tonnes in 2006 (these data pertain to commercial energy plants, industrial energy generating facilities and technologies, but exclude local heat energy generating facilities, household fireplaces, small workshops or agriculture) [1]. These changes have taken place owing to implementation of high-performance dust separators. Such facilities can capture up to 98 % of the ashes produced during combustion processes. However, reduction in the emission of pollutants to air means an increase in amounts of fly ashes stored near power plants. It is estimated that in 2007 about 99.5 % of fly ash produced

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in energy and heat generating plants in Poland was captured and stored. This percentage corresponds to 19,914 thousand tonnes of such waste. Therefore, it is becoming increasingly important to recycle fly ash, a by-product of the energy generating industry. Fly ashes stored in bulk can act as an aggressive factor, adversely affecting ecosystems. However, the same fly ashes contain elements, which can be useful in agricultural practice. Therefore, they can be used as a component added to soil in order to improve its physiochemical properties [2, 3]. Such waste can also be used as fertilizers [3–7]. By introducing fly ashes to soil, it is possible to improve the balance of nutrients in environment and reduce the negative effect of excessive concentration of fly ashes near energy generating plants. The data found in the relevant references largely explain the immediate effect of hard coal fly ashes on the properties of soil and crop yields. In contrast, there is little information regarding the long-term changes caused by introduction of fly ashes to soil.

The results presented in this paper aimed at clarifying how fly ashes from energy generating plants can affect the total nitrogen abundance as well as the content of nitrogen mineral forms, ie ammonia nitrogen and nitrates, in soil. Another objective was to determine the interaction between fly ashes and organic amendments, such as farmyard manure, straw and tree bark, added to soil together with fly ashes. The analyses were performed 19 years after these substances had been introduced to soil, which enabled the authors to evaluate the duration of their influence on the selected forms of nitrogen in soil.

Material and methods

The study was based on a field experiment established in 1884 in the commune of Lelis, in the Mazowia province, on weak rye complex 6 soil. The arable horizon of the soil represented the grain size distribution defined as slightly loamy and silty sand [8]. The soil was moderately abundant in available phosphorus (55 mg P kg^{-1}) and rich in available potassium (152 mg K kg^{-1}) and magnesium (55 mg Mg kg^{-1}). The sorptive capacity of the soil was 12.3 cmol(+) kg^{-1}, and the reaction measured in water and in 1 M KCl was 6.5 and 5.6, respectively.

The experiment was set up according to the random block design with four replications, including three experimental factors. The first order factor consisted of increasing doses of hard coal fly ashes from electrofilters in Ostroleka Power Plant, introduced to soil in the following doses: 0, 100, 200, 400, 600 and 800 Mg $\cdot$ ha^{-1}. The fly ashes used in the experiment contained 491 g SiO_2, 1.7 g P, 2.9 g K, 15.0 g Ca and 7.1 Mg in 1 kg dm. Their reaction pH measured in 1 M KCl was 9.2. The second order factor comprised the organic amendments which were introduced to soil alongside fly ashes. They included farmyard manure (FYM), straw and tree bark, in the amount of 10 Mg dm per 1 ha. The depth of soil profile at which soil samples were collected made up the third order factor. Each plot covered 54 m^2.

Fly ashes and organic amendments were added to soil in the autumn of 1984, before winter ploughing. The crops grown in the subsequent years were potatoes (1985), oat for green matter + lupine for green matter (1987), rye for green matter + a mixture of legumes and grasses for green matter (1987), and a mixture of legumes and grasses for green matter in 1988–1991. All the crops received NPK fertilization in rates recommended in agronomy, identical during the entire experiment. In 1992, the field was used as permanent grassland, without mineral fertilization.

In 2003, nineteen years after fly ashes had been applied, soil samples were taken from particular objects at four depths: 0–25 cm, 26–50 cm, 51–75 cm and 76–100 cm. Samples were collected using a soil drill measuring ∅ = 50 mm in diameter, from four different locations on each plot. These samples were then aggregated as one sample from each plot. Fresh soil collected for analyses was air dried, passed through a sieve of a ∅ = 1.0 mm mesh size. The samples thus prepared underwent the following determinations: total nitrogen by Kjeldahl's method [9], having digested the soil with sulphuric acid in an open system, the content of ammonia nitrogen by colorimetry using Nessler's reagent in a Spekol 220 apparatus at wavelength λ = 410 nm, having previously extracted samples with 1 % K_2SO_4, and the content of nitrate nitrogen by colorimetry using phenyl disulphonic acid [10], likewise in a Spekol apparatus at wavelength λ = 220 nm.

The results were processed statistically applying ANOVA test, at the level of significance α = 0.05, with an aid of the software package Statistica v. 8.0 [11]. The correlation between a dose of fly ashes and the content of $N\text{-}NO_3$ and $N\text{-}NH_4$ was determined using a simple correlation coefficient [12].

Results and discussion

Fly ashes from power plants contain negligible amounts of nitrogen. During coal combustion, this element is released to the atmosphere as oxides. The total nitrogen amounts recorded in fly ashes are less than a few tenths of a per cent [13] and are not any larger source of nitrogen for plants. Nevertheless, the results presented in this paper have proven that application of fly ashes has significantly affected the level of nitrogen in soil. The increasing rates of fly ashes introduced to soil 19 years earlier have caused a highly significant increase in the content of N-total content in soil (Table 1).

Table 1

Total-N content in the soil 19 years after application of hard coal fly ash and organic amendments [g · kg^{-1} dm of soil]

Hard coal fly ash rate [Mg · ha^{-1}]	Organic amendments			
	Without amendments	Farmyard manure	Straw	Tree bark
soil layer 0–25 cm				
0	0.89	0.95	1.03	1.01
100	1.17	1.29	1.23	1.26
200	1.20	1.22	1.26	1.17
400	1.32	1.40	1.21	1.19
600	1.15	1.17	1.12	1.07

Table 1 contd.

Hard coal fly ash rate [Mg · ha^{-1}]	Organic amendments			
	Without amendments	Farmyard manure	Straw	Tree bark
800	1.13	1.17	1.20	1.04
$LSD_{0.05}$ for:	hard coal fly ash rate – 0.020**; organic amendments – 0.017**; hard coal fly ash rate × organic amendments – 0.041**			
correlation coefficient	0.35 ns	0.21 ns	0.15 ns	–0.34 ns
soil layer 26–50 cm				
0	0.14	0.19	0.33	0.36
100	0.84	0.60	0.62	0.36
200	0.24	0.28	0.38	0.36
400	0.47	0.52	0.41	0.30
600	0.30	0.47	0.23	0.27
800	0.32	0.46	0.60	0.34
$LSD_{0.05}$ for:	hard coal fly ash rate – 0.015**; organic amendments – 0.012*; hard coal fly ash rate × organic amendments – 0.030**			
correlation coefficient	–0.15 ns	0.38 ns	0.09 ns	–0.55 ns
soil layer 51–75 cm				
0	0.25	0.20	0.24	0.24
100	0.27	0.27	0.29	0.21
200	0.18	0.20	0.22	0.18
400	0.21	0.21	0.18	0.17
600	0.18	0.18	0.25	0.22
800	0.24	0.20	0.22	0.23
LSD for:	hard coal fly ash rate – 0.022**; organic amendments – 0.018*; hard coal fly ash rate × organic amendments – 0.045*			
correlation coefficient	–0.24 ns	–0.43 ns	–0.28 ns	0.04 ns
soil layer 76–100 cm				
0	0.19	0.18	0.17	0.18
100	0.17	0.18	0.18	0.15
200	0.18	0.21	0.23	0.21
400	0.17	0.19	0.18	0.15
600	0.22	0.20	0.19	0.20
800	0.25	0.19	0.15	0.19
$LSD_{0.05}$ for:	hard coal fly ash rate – ns; organic amendments – ns; hard coal fly ash rate × organic amendments – ns			
correlation coefficient	0.56 ns	0.21 ns	–0.34 ns	0.24 ns

Two-way ANOVA: ** – significant at $\alpha < 0.01$, * – significant at $\alpha < 0.05$, ns – not significant.

Such correlation was most evidently revealed in soil collected from the arable layer 0–25 cm. In the series without added organic amendments, increasing doses of fly ashes have raised the total nitrogen content from 0.89 g N kg^{-1} of soil in the control treatment to 1.32 g N kg^{-1} soil in the object which had received the dose of fly ashes equal 400 Mg ha^{-1}. Higher doses of fly ashes did not lead to further increase in the N-total content. As the depth of sample collecting increased, the total N content declined. In the control series – without added organic amendments – total nitrogen reached 1.14, 0.39, 0.22 and 0.20 g kg^{-1} of soil in the subsequent soil horizons. This effect was accompanied by concomitant disappearance of the effect of the applied fly ashes on total nitrogen in soil. In the deepest soil profile layer, ie 76–100 cm, no effect of the applied fly ashes on the total nitrogen content in soil was determined.

Similarly, additional application of organic amendments had a significant influence on modelling the long-term effect expressed as the total N content in soil. The analysis of variance run with respect to total nitrogen revealed a highly significant dependence of this trait on the applied organic amendments at the depths of 0–15 cm and 26–50 cm. Weaker effect was observed at the depth of 51–75 cm, while at the deepest layer, 76–100 cm, no such effect was evidenced. When analyzing the average values, it has been verified that among the tested organic substances, the total N content in soil was raised versus the control value (1.14 g N kg^{-1}) by FYM (1.20 g N kg^{-1}) and straw (1.18 g N kg^{-1}). Tree bark, in contrast, depressed the total N content (1.12 g N kg^{-1}).

Although fly ashes alone do not contain nitrogen as a fertilizer component, over the many years they have contributed to an increase in the content of nitrogen in soil. This effect is attributable to improved growing conditions for plants, created by fly ashes and their properties. Under such improved conditions lasting for many years, owing to deeper and more intensive root development the soil naturally gathered more post-harvest residue, which is now a valuable source of available nitrogen to aftercrops. The fact that N-total increases in soil following application of fly ashes has been also demonstrated by Kawecki and Tomaszewska [14, 15], Giedrojc and Fatyga [16] and Wojcieszczuk et al [17].

The fly ashes tested in this experiment had a significant effect on the content of nitrate nitrogen in soil (Table 2).

When comparing the soil profile horizons, it became evident that the content of N-NO_3 was the highest in the soil's arable layer, 0–25 cm deep. In the control series (with no amendments added to soil), it ranged from 2.32 to 4.57 mg kg^{-1} of soil. Analogously to total N, the content of this form of nitrogen tended to decline in deeper layers of soil and the influence produced by application of fly ashes on this form of nitrogen in soil weakened. In the deepest layer, 75–100 cm, no effect of fly ashes on the content of N-NO_3 in soil was determined.

In the arable layer of soil, the highest content of nitrates was found in the series with added tree bark, on average 4.07 mg N-NO_3 kg^{-1}. Less N-NO_3 appeared in the series supplemented with straw (3.64 mg kg^{-1} soil) and the lowest content of this form of nitrogen was determined in the objects treated with farmyard manure (3.46 mg kg^{-1} soil).

Table 2

N-NO_3 content in the soil 19 years after application of hard coal fly ash and organic amendments [mg · kg^{-1} dm of soil]

Hard coal fly ash rate [Mg · ha^{-1}]	Organic amendments			
	Without amendments	Farmyard manure	Straw	Tree bark
soil layer 0–25 cm				
0	2.32	2.69	2.33	3.93
100	3.75	3.15	3.80	3.76
200	3.75	3.67	4.08	4.25
400	4.57	4.40	4.27	4.43
600	4.57	3.89	3.59	4.20
800	4.00	2.98	3.75	3.86
$LSD_{0.05}$ for:	hard coal fly ash rate – 0.65**; organic amendments – ns; hard coal fly ash rate × organic amendments – ns			
correlation coefficient	0.64 ns	0.16 ns	0.34 ns	0.12 ns
soil layer 26–50 cm				
0	1.94	2.41	2.16	2.75
100	2.86	3.48	1.34	1.55
200	1.26	1.71	1.06	1.29
400	1.43	2.38	1.61	1.42
600	1.07	1.20	1.10	1.53
800	1.09	2.69	1.80	1.72
$LSD_{0.05}$ for:	hard coal fly ash rate – 0.37**; organic amendments – 0.30**; hard coal fly ash rate × organic amendments – 0.74**			
correlation coefficient	–0.67 ns	–0.24 ns	–0.12 ns	–0.38 ns
soil layer 51–75 cm				
0	2.62	1.23	1.03	2.61
100	1.41	1.79	2.01	2.55
200	2.91	1.75	1.91	1.12
400	0.95	1.16	2.25	1.67
600	1.88	2.28	1.21	1.83
800	1.80	1.71	1.08	1.22
LSD for:	hard coal fly ash rate – ns; organic amendments – ns; hard coal fly ash rate × organic amendments – 1.27*			
correlation coefficient	–0.28 ns	0.25 ns	–0.22 ns	–0.57 ns
soil layer 76–100 cm				
0	1.74	3.21	1.77	2.89
100	1.85	1.69	1.95	1.62
200	1.48	0.93	0.59	1.26
400	1.53	1.34	1.23	2.30
600	1.60	1.70	1.86	2.30
800	1.21	1.94	2.16	1.95
$LSD_{0.05}$ for:	hard coal fly ash rate – 0.48**; organic amendments – 0.39*; hard coal fly ash rate × organic amendments – ns			
correlation coefficient	0.36 ns	0.00 ns	0.06 ns	0.02 ns

Two-way ANOVA: ** – significant at $\alpha < 0.01$, * – significant at $\alpha < 0.05$, ns – not significant.

The content of ammonia nitrogen in soil was varied and depended on such factors as a rate of fly ashes, the applied organic substance and the depth of collecting soil samples (Table 3).

Table 3

$N\text{-}NH_4$ content in the soil 19 years after application of hard coal fly ash and organic amendments [$mg \cdot kg^{-1}$ dm of soil]

Hard coal fly ash rate [$Mg \cdot ha^{-1}$]	Organic amendments			
	Without amendments	Farmyard manure	Straw	Tree bark
soil layer 0–25 cm				
0	8.82	8.00	10.28	6.77
100	7.69	9.27	9.78	7.77
200	11.36	10.72	12.00	7.23
400	11.94	11.56	12.85	11.02
600	13.79	16.79	14.66	14.29
800	13.83	13.68	12.67	12.09
$LSD_{0.05}$ for:	hard coal fly ash rate – 1.50**; organic amendments – 1.22**; hard coal fly ash rate × organic amendments – ns			
correlation coefficient	0.85 ns	0.77 ns	0.66 ns	0.88 ns
soil layer 26–50 cm				
0	9.37	8.70	10.24	9.78
100	5.89	6.61	6.00	6.11
200	7.04	6.42	7.33	6.62
400	6.09	6.94	5.45	6.99
600	5.29	6.05	7.06	7.06
800	6.68	6.00	5.69	5.80
$LSD_{0.05}$ for:	hard coal fly ash rate – 0.77**; organic amendments – ns; hard coal fly ash rate × organic amendments – ns			
correlation coefficient	–0.52 ns	–0.59 ns	–0.54 ns	–0.51 ns
soil layer 51–75 cm				
0	10.65	12.68	11.33	10.15
100	11.08	10.66	10.47	9.52
200	8.00	8.53	7.56	5.75
400	6.18	4.72	7.58	7.02
600	7.19	4.19	5.88	7.02
800	6.88	5.79	3.33	4.17
LSD for:	hard coal fly ash rate – 1.16**; organic amendments – ns; hard coal fly ash rate × organic amendments – 2.33*			
correlation coefficient	–0.73 ns	–0.83 ns	–0.92 ns	–0.74 ns
soil layer 76–100 cm				
0	5.15	7.20	4.34	4.39
100	4.48	4.99	4.10	4.71
200	4.61	5.67	6.57	7.00

Table 3 contd.

Hard coal fly ash rate [Mg · ha^{-1}]	Organic amendments			
	Without amendments	Farmyard manure	Straw	Tree bark
400	3.76	4.16	4.37	3.72
600	4.93	6.80	3.50	4.50
800	6.57	6.34	4.97	6.07
$LSD_{0.05}$ for:	hard coal fly ash rate – ns; organic amendments – ns; hard coal fly ash rate × organic amendments – ns			
correlation coefficient	0.46 ns	0.06 ns	–0.09 ns	0.09 ns

Two-way ANOVA: ** – significant at $\alpha < 0.01$, * – significant at $\alpha < 0.05$, ns – not significant.

Fly ashes evidently, in a nearly linear fashion, raised the content of this form of nitrogen in the series without additional organic amendments and in the series fertilized with manure or tree bark up to 600 Mg ha^{-1}. Such dependence was not confirmed for the series with straw, although straw introduced to soil resulted in the highest mean accumulation of N-NH_4 in soil (12.04 mg kg^{-1}). In the series with FYM, the determined concentration of ammonia nitrogen was 11.67 mg kg^{-1}, while in the control treatment, this amount reached 11.24 mg kg^{-1}. Tree bark strongly reduced the amount of N-NH_4, down to 9.86 mg kg^{-1}. The influence of fly ashes added to soil 19 years earlier on ammonia nitrogen was observable down to the depth of 51–75 cm, although the dependence between a dose of fly ashes and the content of N-NH_4 in this soil layer was reverse. Higher levels of ammonia nitrogen were found in the plots which had received smaller doses of fly ashes. In the deepest layer, 76–100 cm, none of the dependences mentioned above occurred.

The present study has demonstrated that N-NH_4 prevailed over N-NO_3 in soil collected from all the treatments. These observations are divergent from the literature data, which imply a reverse dependence, ie prevalence of nitrates over the ammonia form of nitrogen [18]. The prevalence of ammonia form over nitrates is typical for soils in Poland. This fact proves that there are conditions which limit the nitrification process [19, 20].

Conclusions

1. Hard coal fly ashes and organic amendments added to soil together with ashes have contributed to the increase in the analyzed forms of nitrogen in soil, mainly in its arable horizon.

2. Among the tested organic amendments, irrespective of the depth of collecting soil samples, tree bark had the strongest effect on the content of N-NO_3, raising its concentration in soil.

3. Regarding N-NH_4, the most desirable effect was produced by straw as a soil amending substance, as it depressed the level of this form of nitrogen in soil.

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NASTĘPCZE ODDZIAŁYWANIE POPIOŁÓW Z WĘGLA KAMIENNEGO NA ZAWARTOŚĆ AZOTU W GLEBIE

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Abstrakt: Pracę poświęcono wyjaśnieniu następczego oddziaływania popiołów z węgla kamiennego na zawartość wybranych form azotu w glebie. Badania wykonano, korzystając z doświadczenia polowego po 19 latach od jego założenia. Popioły stosowano w dawkach 0, 100, 200, 400, 600 i 800 Mg $\cdot$ ha^{-1} z uwzględnieniem czterech serii: bez dodatku substancji organicznej, z obornikiem, ze słomą i z korą drzewną. Uzyskane wyniki badań wskazują, że popioły z węgla kamiennego oraz wprowadzane wraz z nimi dodatki nawozów organicznych znacznie wpłynęły na długookresowe kształtowanie się zawartości badanych form azotu w glebie. Działanie popiołów uwidoczniło się przede wszystkim w warstwie ornej badanej gleby. W głębszych warstwach nie stwierdzono wpływu popiołów na zmiany zawartości badanych form azotu. Spośród zastosowanych dodatków organicznych niezależnie od poziomu pobrania próbek gleby na zawartość N-NO_3 najsilniej wpływała kora drzewna, powodując wzrost jego ilości. W odniesieniu do formy N-NH_4 najsilniejszy wpływ na zawartość tej formy azotu miała słoma.

Słowa kluczowe: popioły lotne z węgla kamiennego, azot, N-amonowy, N-azotanowy

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QUANTITATIVE ABILITIES OF BIOLOGICAL NITROGEN REDUCTION FOR *Rhizobium galegae* CULTURES BY GOAT'S RUE

ILOŚCIOWE MOŻLIWOŚCI BIOLOGICZNEJ REDUKCJI AZOTU PRZEZ BAKTERIE *Rhizobium galegae* WSPÓŁŻYJĄCE Z RUTWICĄ WSCHODNIĄ

Abstract: The field experiment (microplots) was carried out in 2005–2007 in the experimental site belonging to the University of Podlasie in Siedlce. Nitrogen ^{15}N at 10.3 at. % enrichment was applied in a form of $(^{15}NH_4)_2SO_4$ at the amount of 1.66g per 1 m^2 in early spring. In parallel to goat's rue (*Galega orientalis* Lam.) cultivation, also plant that did not show the ability of biological N_2 reduction (spring barley (*Hordeum sativum*) was grown, and it was also fertilized with ^{15}N in the form of $(^{15}NH_4)_2SO_4$ at 10.3 at. % enrichment.

The quantitative abilities of biological nitrogen reduction for *Rhizobium galegae* cultures living together by goat's rue (*Galega orientalis* Lam.) was determined by means of isotope dilution method. The abundance of at. % ^{15}N was determined by spectroscopic method on the spectrophotometer NOI – 6E, then the amount of nitrogen transferred from the air due to biological N_2 reduction process, was calculated.

The yield of as a sum from three cuts of dry matter of tested plant in subsequent study years was [kg $\cdot$ m^{-2}]: 2005 – 1.092; 2006 – 0.831; 2007 – 0.509. The quantity of biologically reduced nitrogen reached up the mean value for three experimental years at the level of 28.863 g N $\cdot$ m^{-2} but in each year as follows [g N $\cdot$ m^{-2}]: 2005 – 37.603; 2006 – 26.080; 2007 – 22.906 during the whole vegetation period.

Keywords: *Rhizobium galegae* cultures, goat's rue, yield, spring barley

High prices of nitrogen fertilizers considerably increase the costs of animal fodder production. However, there is an opportunity to decrease them due by cultivating the fodder plant species that have the ability of biological N_2 reduction [1]. The goat's rue (*Galega orientalis* Lam.) can be the example.

Process of biological reduction of gaseous nitrogen from atmospheric air consists its incorporating into the biological system [2, 3]. *Rhizobium* bacteria living in a symbiosis with papilionaceous plants, as well as freely living bacteria (*Azotobacter, Clostridium*), fungi (*Rhizopus*), and actinomycetes (*Streptomyces*), show such ability [4, 5]. Their

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common feature is that they contain nitrogenase – a principle enzyme responsible for elemental nitrogen reduction. Nitrogenase is composed of two protein complexes. Protein containing Mo-Fe is the enzyme that reduces N_2, while protein containing only Fe provides with electrons necessary for reduction process.

Recently, more and more intensive studies are performed upon the goat's rue (perennial papilionaceous plant species) originating from Caucasus or Estonia [6, 7, 8, 9]. The plant can be grown for green forage, dried fodder, protein concentrate, and as energetic plant [10]; it can also be used for conserving potential wastelands.

The present study aimed at evaluating the amount of nitrogen from air biologically reduced by goat's rue biomass (*Galega orientalis* Lam.) during three subsequent vegetation periods.

Material and methods

The field experiment (microplots) was conducted in 2005–2007 on goat's rue plantation (9th, 10th, and 11th years of cultivation). Studies were carried out on a soil developed from strong loamy sand at pH value 6.9 in 1 mol KCl dm^{-3}. The experiment was performed on soil which contained 31.2 $g \cdot kg^{-1}$ of total carbon and 3.6 $g \cdot kg^{-1}$ of total nitrogen. Its abundance in available phosphorus and potassium was considered as moderate, while magnesium – poor. Nitrogen ^{15}N at 10.3 at. % enrichment was applied in a form of $(^{15}NH_4)_2SO_4$ at the amount of 1.66 g per 1 m^2 in early spring. Along with the goat's rue (*Galega orientalis* Lam.), also other plant that had not the feature of gaseous nitrogen reduction, was cultivated (spring barley – *Hordeum sativum*), and it was also fertilized with ^{15}N in form of $(^{15}NH_4)_2SO_4$ at 10.3 at. % enrichment.

Each year of study, three cuts of the test plant were harvested at the budding stage. The fresh and dry matter yields were determined. During the harvest of subsequent cuts of goat's rue (*Galega orientalis* Lam.), whole plant samples were collected, and they were dried and ground. Total nitrogen content was determined by means of Kjeldahl's method after wet digestion [4]. Analogous procedure was applied to spring barley as a control plant.

The quantitative abilities of biological nitrogen reduction by goat's rue were evaluated be means of isotope dilution method using spectrophotometer NOI – 6E for determination of (at. % ^{15}N), then the amount of nitrogen from the air due to biological reduction of gaseous nitrogen, was calculated [4]. Percentage of nitrogen plant from air calculated according to model [5]:

$$\% \text{ N} = [1 - (\text{at. } \% \text{ } ^{15}\text{N enrichment fx : at. } \% \text{ } ^{15}\text{N enrichment nfx})] \cdot 100$$

fx – papilionaceous plant, nfx – non-papilionaceous plant.

Achieved results were statistically processed applying variance of analysis, whereas significant differences were calculated using Tukey's test at the significance level of $p = 0.05$.

Results and discussion

Data on rainfalls and air temperatures during vegetation seasons 2005–2007 are presented in Table 1.

Table 1

Air temperatures and rainfall in the vegetation in the years 2005–2007.
Reported by the measurement centre in Siedlce

Means air temperature [^{o}C]								
Months	Years	IV	V	VI	VII	VIII	IX	Mean
Mean monthly	2005	8.6	13.0	15.9	20.2	17.5	15.0	15.0
	2006	8.4	13.6	17.2	22.3	18.0	15.4	15.8
	2007	8.3	14.5	18.2	18.5	18.6	13.1	15.2
Multiyear mean		7.7	10.0	16.1	19.3	18.0	13.0	11.4
Total monthly rainfall [mm]								Sum
Sum monthly	2005	12.3	64.7	44.1	86.5	45.4	15.8	268.8
	2006	29.8	39.6	24.0	16.2	227.6	22.0	359.2
	2007	21.2	59.1	59.9	70.2	31.1	67.6	309.1
Multiyear sum		52.3	50.0	68.2	45.7	66.8	60.7	343.7

Mean monthly temperature in subsequent vegetation periods was similar (15.0 to 15.8 ^{o}C), which was much higher as compared to many-year average. Temperatures recorded during vegetation favored the process of biological reduction of N_2 [11]. Mean sum of rainfalls during vegetation was lower than the many-year value. Only in 2006, it was slightly higher (by 15.5 mm), which resulted from high precipitation sum in August 3-fold exceeding the many-year average level.

Mean yield of dry matter biomass of goat's rue (*Galega orientalis* Lam.) harvested at budding stage amounted to 0.878 kg $\cdot$ m^{-2}, which was significantly differentiated for studied factors, as well as their interaction (Table 2). Significantly the highest yields were achieved for the I cut. For subsequent cuts of goat's rue, a considerable decrease of yields was recorded. When considering subsequent study years, it can be univocally concluded that the highest yield of the test plant was harvested in 2005 (1.092 kg $\cdot$ m^{-2}), whereas it decreased by about 100% in the third year. Mean nitrogen content in goat's rue biomass (*Galega orientalis* Lam.) was 37.4 g $\cdot$ kg^{-1} dm (Table 2). Here achieved results upon nitrogen contents are similar to those recorded by Ignaczak [6] for the first and second cuts. Symanowicz and Kalembasa [8], in the field experiment involving goat's rue seeds infected by *Rhizobium galegae*, determined slightly higher total nitrogen amounts (39.0–43 g $\cdot$ kg^{-1} dm). In other study with goat's rue, in which nitrogen contents in the plant biomass were compared in the third and seventh cultivation years [12], mean nitrogen content at budding stage ranged around 29.3 g $\cdot$ kg^{-1} dm in the third and 48.1 g $\cdot$ kg^{-1} dm in the seventh year. However, in the pot experiment, Andrzejewska and Ignaczak [7] observed lower nitrogen concentrations in aboveground parts of goat's rue (0.81–2.33 %). Probably, the field conditions are more favorable for biological reduction of N_2. Significantly the highest nitrogen content was determined in the first cut. Subsequent study years affected the total nitrogen content in the biomass at the level of about 39.2–37.8 g · kg^{-1} dm).

Table 2

Yield of dry matter [kg · m^{-2}] and the content of total nitrogen [g · kg^{-1}] of got's rue (*Galega orientalis* Lam.) of fertilization ^{15}N

Cuts (A)	Dry matter yield [kg · m^{-2}]				Nitrogen content [g · kg^{-1}]			
	Research years (B)							
	2005	2006	2007	Mean	2005	2006	2007	Mean
I	0.772	0.557	0.270	0.533	47.2	41.6	41.6	43.5
II	0.276	0.140	0.273	0.230	33.6	30.4	33.6	32.5
III	0.044	0.134	0.166	0.115	36.7	33.9	38.1	36.2
Sum (Mean)	1.092	0.831	0.509	0.878	39.5	35.3	37.8	37.4
$LSD_{0.05}$ for:								
cuts (A)	0.005				1.4			
years (B)	0.005				1.4			
interaction (A×B)	0.009				2.5			

A summarized nitrogen uptake along with the three cuts of goat's rue dry matter was 35.343 g N · m^{-2} (Table 3). Significant differences in nitrogen uptake were present between subsequent cuts and study years as well as interaction of these factors. Significantly the highest nitrogen uptake with goat's rue biomass yield (23.614 g N · m^{-2}) was recorded for the first cut, and it reached up to about 3-fold higher level in relation to that for the second cut.

Table 3

Uptake of nitrogen in the yield of dry matter of goat's rue [g N · m^{-2}] and at. % ^{15}N enrichment

Cuts (A)	Uptake [g N · m^{-2}]				At. % ^{15}N enrichment			
	Research years (B)							
	2005	2006	2007	Mean	2005	2006	2007	Mean
I	36.438	23.171	11.232	23.614	0.037	0.035	0.039	0.037
II	9.274	4.256	9.173	7.568	0.017	0.019	0.018	0.018
III	1.615	4.543	6.325	4.161	0.009	0.011	0.011	0.010
Sum (Mean)	47.327	31.970	26.730	35.343	0.021	0.022	0.023	0.023
$LSD_{0.05}$ for:								
cuts (A)	0.262				0.01			
years (B)	0.262				ns			
interaction (A×B)	0.453				ns			

A considerable decrease of nitrogen uptake with goat's rue dry matter occurred in subsequent years. Particular cuts and subsequent study years differentiated the nitrogen uptake. Significantly the lowest nitrogen uptake was calculated for the third cut. Table 3 also presents the atomic enrichment percentage (at. % ^{15}N enrichment) for particular cuts and years. These values were calculated from the difference between the nitrogen amount expressed as at. % ^{15}N of examined sample and a standard (nitrogen contained in the air – 0.3663 % ^{15}N). Statistical processing revealed significant differentiation of the enrichment with ^{15}N isotope at goat's rue only for cuts.

The highest isotope ^{15}N enrichment was recorded for the first cut in subsequent study years (0.037, on average). In the second and third cut, the enrichment value decreased reaching its minimum levels in the last cut. It can be supposed that lower ^{15}N enrichment was associated with its dissolution in goat's rue yields. The ^{15}N isotope enrichment was also determined at spring barley (as a control plant) that has not the ability of biological gaseous nitrogen reduction. The value was – 0.214.

The percentage of total nitrogen share at goat's rue (*Galega orientalis* Lam.) due to biological reduction of atmospheric nitrogen was significantly differentiated for cuts and experimental years (Table 4). The highest values were achieved for the third cut (90.9%).

Table 4

Percentage share of total nitrogen from the air as a result of biological reduction of N_2 and amount of nitrogen biologically reduced for *Rhizobium galegae* cultures living together by goat's rue [g N · m^{-2}]

Cuts (A)	% total N from biological reduction of N_2				Amount of nitrogen biologically reduced from air [g N · m^{-2}]			
	Research years (B)							
	2005	2006	2007	Mean	2005	2006	2007	Mean
I	82.7	79.3	81.6	812	28.034	18.375	9.165	18.525
II	92.0	87.1	88.5	89.2	8.133	3.707	8.118	6.653
III	95.8	88.0	88.9	90.9	1.436	3.998	5.623	3.686
Sum (Mean)	90.2	84.5	86.3	87.1	37.603	26.080	22.906	28.863
LSD $_{0.05}$ for:								
cuts (A)	3.01				0.072			
years (B)	3.01				0.072			
interaction (A×B)	ns				0.125			

A high percentage of total nitrogen due to biological reduction was confirmed in studies by Andrzejewska and Ignaczak [7].

During its whole vegetation season of the goat's rue the biological reduction of nitrogen from air reached 28.863 g N · m^{-2} from the air (Table 4). Studied factors as well as their interaction significantly differentiated the amount of nitrogen uptaken from the air. The highest quantities of biologically reduced nitrogen were determined in the biomass of the first cut of goat's rue harvested at budding stage. The highest summarized amounts of nitrogen for the three cuts were recorded in the first study year – 2005 (37.603 g N · m^{-2}). Achieved results were similar to those reported by Symanowicz et al [13], in which the amounts of biologically reduced nitrogen by goat's rue harvested at budding stage were 379.7 kg N · ha^{-1}. Calculated correlation coefficient (r = 0.99) indicated the dependence between the quantity of biologically reduced nitrogen in subsequent cuts and experimental years.

Conclusions

1. The harvest of the first cut of goat's rue (*Galega orientalis* Lam.), significantly pointed out the highest values for biomass yield, total nitrogen content, nitrogen uptake, at. % ^{15}N enrichment, and biologically reduced nitrogen amounts were recorded.
2. Significant decrease of studied parameters occurred in subsequent experimental years.
3. Mean amount of biologically reduced nitrogen during the whole vegetation period of goat's rue (*Galega orientalis* Lam.) was 28.863 g N · m^{-2}.

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ILOŚCIOWE MOŻLIWOŚCI BIOLOGICZNEJ REDUKCJI AZOTU PRZEZ BAKTERIE *Rhizobium galegae* WSPÓŁŻYJĄCE Z RUTWICĄ WSCHODNIĄ

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Abstrakt: Doświadczenie polowe mikropoletkowe przeprowadzono w latach 2005–2007 na polu należącym do Akademii Podlaskiej w Siedlcach. Azot ^{15}N o wzbogaceniu 10,3 at. % stosowano w formie $^{15}(NH_4)_2SO_4$ w ilości 1,66 g na 1 m^2 wczesną wiosną. Równolegle z uprawą rutwicy wschodniej (*Galega orientalis* Lam.) uprawiano roślinę niemającą zdolności biologicznej redukcji N_2 (jęczmień jary – *Hordeum sativum*), którą również nawożono ^{15}N w formie $^{15}(NH_4)_2SO_4$ o wzbogaceniu 10,3 at. %.

Ilościowe możliwości biologicznej redukcji azotu przez kultury bakterii *Rhizobium galegae* współżyjące z rutwicą wschodnią (*Galega orientalis* Lam.) określono po zastosowaniu metody izotopowego rozcieńczenia.

Na spektrofotometrze NOI – 6E oznaczono at. % ^{15}N, a następnie obliczono ilość azotu pochodzącego z powietrza w wyniku biologicznej redukcji N_2.

Sumaryczny plon suchej masy rośliny testowej w kolejnych latach badań wynosił [kg · m^{-2}]: 2005 – 1,092; 2006 – 0,831; 2007 – 0,509. Ilość biologicznie zredukowanego azotu osiągnęła średnią wartość z trzech lat badań na poziomie 28,863 g N · m^{-2}, a w kolejnych latach kształtowała się następująco [g N · m^{-2}]: 2005 – 37,603; 2006 – 26,080; 2007 – 22,906 w ciągu okresu wegetacyjnego.

Słowa kluczowe: bakterie *Rhizobium galegae*, rutwica wschodnia, plon, jęczmień jary

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CUMULATION OF BIOLOGICALLY REDUCED NITROGEN IN THE BIOMASS OF YELLOW LUPINE (*Lupinus luteus*) AT ITS DIFFERENT GROWING STAGES

KUMULACJA BIOLOGICZNIE ZREDUKOWANEGO AZOTU PRZEZ ŁUBIN ŻÓŁTY (*Lupinus luteus*) W RÓŻNYCH JEGO FAZACH ROZWOJOWYCH

Abstract: The content of biological reduced nitrogen from air by yellow lupine (*Lupinus luteus*) living in the symbiosis with *Rhizobium lupine* which biomass was harvested in differentiated developing stages was determinated in pot experiment. The highest share in total yield of yellow lupine harvested in the blooming stage were leaves (51.4 %) but at full maturity steams (45.7 %). The roots of tested plant were in relation to total yield 14.7 % harvested at first term and 6.7 % at second term. The total yield of yellow lupine harvested at the stage of full maturity was almost twofold higher that at blooming stage. The content of total nitrogen in vegetative parts of yellow lupine was, the highest in the leaves and in roots and steams was about 1/3 lower than in leaves but in and seeds nearly two and three times higher that in leaves, relatively. The enrichment in ^{15}N in particularly parts of mustard (plant which takes up nitrogen only from two sources, namely from fertilizer and soil) was higher in comparison with relatively parts of yellow lupine (which is able to take up the nitrogen from three sources: fertilizer, soil and atmospheric air). The share of nitrogen which was biologically reduced in the total content of those element got lured in biomass of roots, steams and leaves harvested at blooming stages reached respectively 9.8; 16.9 and 59.8 % (total in the whole plant 43.2 %). In the biomass of yellow lupine harvested at maturity stage the share of nitrogen coming form the biological reduction process in the total amount of those element cumulated in roots, steams, leaves, stripped pods and seeds reached 6.7; 22.8; 26.0; 26.6 and 35.6 % respectively (total the in whole plant 29.2 %). In total amount of nitrogen coming from different sources the amount of this element taken up by yellow lupine reached from: fertilizer 23.1 % in blooming stage and 31.3 % in full maturity stage, but the share of nitrogen taken up from soil reached 83 % at the first term and 38.9 % in the second term of harvesting.

Keywords: nitrogen, the biological reduction of nitrogen by plant, yellow lupine, white mustard, isotope ^{15}N

Introducing the legume family crops living in a symbiosis with *Rhizobium* genus bacteria into the crop rotation system, is the most energy-saving and efficient form (besides natural and organic fertilizers) of nitrogen nutrition that allows for considerable

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reductions in the element amounts introduced into the soil environment in a form of mineral fertilizers [1].

During the last twenty years, the area of legume family crops cultivation has been gradually decreasing to the advantage of cereals. Current percentage of these crops in sown structure in Poland is less than 1 %. Import of the crushed soybean seed as a cheaper protein source along with instability of legume family crops yielding due to the surplus of vegetative over generative organs greatly affect the poor popularity of these plants. However, domestic legume family plant species should play a major role when popularizing the high-quality, natural, and genetically non-modified food for people and fodder for animals. Moreover, that group of crops has out-of-production virtues manifesting as the improvements in soil fertility and its abundance in nutrients, mainly nitrogen. Ability to bind atmospheric nitrogen reduces inputs associated with nitrogen nutrition, both papilionaceous and consequent crops [2–4]. At promoting the balanced agriculture development and caring the natural environment, problems of elevated nitrogen quantities, namely its mineral or readily mineralizable forms in soils, attracts more and more attention. Amount of nitrogen bound within biological reduction processes depends on many natural and anthropogenic factors, including: crop species (even the variety), *Rhizobium* genus bacteria presence, nitrogen nutrition, temperature, rainfalls, and their distribution during vegetation season. Elevating the nitrogen content in the soil where plants binding atmospheric nitrogen grow, depends on their purpose. Considerably large amounts of the element may be introduced into the soil in the case of plants grown for green forage. Then, nitrogen from biological reduction should be taken into account at balancing the nitrogen fertilization not to let its excessive accumulation in soil and cultivated consequent crops.

Yellow lupine may be a plant utilized for many ways. Its green matter harvested at flowering stage has significant nutritional value, because lignifications processes begins when pods are formed [5]. Moreover, the species can be considered as a green fertilizer, which can be completely ploughed or seeds can be harvested at full maturity stage, while post-crop remains introduced into the soil.

The study aimed at evaluating the biologically reduced gaseous nitrogen amounts by yellow lupine (*Lupinus luteus)* growing in a symbiosis with *Rhizobium lupini* bacteria, harvested at various growth and development stages.

Material and methods

The yellow lupine (cv. Parys) was grown in pots of 10 dm^3 capacity and filled with 10 kg of soil (5 plants $\cdot$ pot^{-1}); pots were placed in a greenhouse. In order to determine the amount of nitrogen bound during biological reduction, the isotope dilution method was applied, which required to use mineral fertilizers amended with ^{15}N isotope, along with parallel cultivation of the control plants that have not the ability of symbiosis with nodule bacteria. White mustard (cv. Rota) was the control. Nitrogen fertilization was applied before seed sowing at the amount of 1 g N $\cdot$ pot^{-1}, while phosphorus and potassium at such quantities to achieve N:P:K ratio 1:0.3:1. Phosphorus and potassium were applied in forms of triple superphosphate and potassium salt, whereas nitrogen was introduced as ammonia sulfate enriched with ^{15}N 10.0 at. % isotope. Applying the fertilizer with elevated ^{15}N isotope content allowed for determining the quantity of nitrogen uptaken by lupine from different sources (air, fertilizer, soil resources). Before sowing, lupine seeds were dressed using anti-fungal preparation Dithane M-45 80 WP as well as nitragine containing symbiotic bacteria *Rhizobium lupini*. The soil used in the experiment had granulometric composition of light loamy sand; pH in KCl was 5.2; total nitrogen content 0.81 $g \cdot kg^{-1}$, and organic carbon content 9.0 $g \cdot kg^{-1}$.

Lupine and mustard were harvested at lupine's blooming stage (date I) as well as full maturity of both crops (date II). Collected plant material was divided into roots, stems, and leaves, whereas additionally at full maturity stage, into seeds and pods or hulls. Water content was determined in collected material. Achieved yields were recalculated onto dry matter content. Total amounts of nitrogen, enrichment in ^{15}N isotope, and quantity of nitrogen uptaken by particular parts of yellow lupine from various sources, were calculated according to method given by Kalembasa [6].

Achieved study results were subjected to variance analysis in completely randomized design (F-Fischer–Snedecor test), while $LSD_{0.05}$ to compare mean values were calculated using Tukey test.

Results and discussion

Leaves made up the largest percentage in yellow lupine biomass (Table 1) harvested at flowering stage (51.4%), while stems – at full maturity stage (45.7 %).

Table 1

The yield of yellow lupine [$g\ dm \cdot pot^{-1}$]

Harvesting stage	Part of plant					Total yield
	roots	stems	leaves	stripped pods	seeds	
Flowering stage	2.11 *14.7**	4.86 *33.9**	7.36 *51.4**	— —	— —	14.33
Full maturity stage	1.79 *6.7**	12.27 *45.7**	10.56 *39.3**	1.65 *6.1**	0.59 *2.2**	26.86
Average	1.95	8.57	8.96	—	—	—
$LSD_{0.05}$	ns	3.51	ns	—	—	9.63

* Proportional (%) participation in total yield.

Roots of the plant made up 14.7 % of the total yield on date I, whereas 6.7 % at date II. Weight of yellow lupine roots collected at full maturity was slightly lower than at blooming stage, while for leaves the dependencies were opposite, and in both cases the differences between mean values were not statistically proven. Only the stem weight harvested at date II was significantly higher than at date I. Total yield of lupine harvested at full maturity stage was almost twice as high as at flowering stage. Literature data also underline considerable share of stems and leaves at the initial growth period, while at full maturity stage, seeds play significant role in accumulating dry matter by yellow lupine [7, 8]. In present study, lupine's generative parts (seeds and pods) made up 8.3 % of the total yield. Low seed percentage in the yield was reflected in great failures of the plant cultivation for seeds [9]. A necessary condition leading to the increase of lupine cultivated area should consist in intensive breeding works tending improve the fertility and stability of the plant yielding in years with varied agricultural and climatic conditions [10].

Among vegetative parts of lupine plants, leaves contained the largest amounts of total nitrogen, regardless of the harvest date (Table 2). Nitrogen content in roots and stems was about 1/3 lower than in leaves, while in pods and seeds, it was about two and three times higher than in leaves. Nitrogen content in leaves increases till all leaves are developed and it begins to gradually decrease just before plant blooming [11]. Own study confirmed higher nitrogen contents in leaves, stems, and roots of lupine plants harvested at flowering rather than full maturity stage. The phenomenon should be attributed to the damage of root nodules, which progresses after flowering, as well as transport of nitrogen from vegetative to generative parts of plants – pods and seeds [12].

Table 2

The content of nitrogen in yellow lupine [$g \cdot kg^{-1}$ dm]

Harvesting stage	Part of plant					Average arithmetical
	roots	stems	leaves	stripped pods	seeds	
Flowering stage	20.9	20.7	33.4	—	—	25.0
Full maturity stage	17.0	16.7	27.1	49.0	70.0	36.0
Average	19.0	18.7	30.3	—	—	—
$LSD_{0.05}$	2.6	3.0	2.8	—	—	1.7

Enriching particular parts of white mustard (plant that uptakes nitrogen only from two sources: fertilizer and soil) in ^{15}N was higher as compared with corresponded parts of lupine plants (that additionally uptakes nitrogen from the air) (Table 3). The quantity of ^{15}N isotope determined in lupine biomass harvested at full maturity stage was higher than at flowering stage, which indicates the elevated amounts of uptaken nitrogen from a fertilizer, as well as slower rate of biological reduction process.

Table 3

Enrichment ^{15}N isotope of nitrogen in yellow lupine and white mustard [% ^{15}N]

Cultivation plant	Harvesting stage	Part of plant					Average arithmetical
		roots	stems	leaves	stripped pods, siliques	seeds	
Yellow lupine	flowering stage	2.779	3.207	1.939	—	—	2.642
	full maturity stage	3.136	3.441	3.433	3.414	3.142	3.313
Average		2.698	3.040	2.686	—	—	—
White mustard	flowering stage	3.079	3.861	4.825	—	—	3.922
	full maturity stage	3.362	4.456	4.641	4.651	4.876	4.397
Average		3.221	4.158	4.733	—	—	—

Regardless the harvest date, the largest amounts of total nitrogen were accumulated by lupine in leaves, which confirms the assumption on accumulating majority of macronutrients in aboveground biomass by papilionaceous plant species [13]. Percentage of nitrogen originating from biological reduction of gaseous N_2 in its total amount uptaken by roots, stems, and leaves collected at flowering stage was: 9.8, 16.9, and 59.8 %, respectively (or 43.2 % for the whole plant). At full maturity stage, the share of nitrogen from biological reduction in its total quantity accumulated in roots, stems, leaves, and seeds amounted to: 6.7, 22.8, 26.0, 26.6, and 35.6 % (or 29.2 % for the whole plant). In the total amount of nitrogen originating from all sources, its quantities uptaken by lupine plants from fertilizers made up 23.1 % at blooming and 31.9 % at full maturity stage, whereas the share of nitrogen originating from the soil resources made up 33.7 % at date I and 38.9 % at date II of the harvest (Table 4).

Table 4

The quantity of nitrogen taken up through yellow lupine [$mg \cdot pot^{-1}$]

Harvesting stage	Source of nitrogen	Part of plant					Sum
		roots	stems	leaves	stripped pods	seeds	
Flowering stage	biologically reduction N_2	4.2 *9.8**	17.0 *16.9**	146.4 59.8*	—	—	167.7 *43.2**
	fertilizer	11.8 *27.2**	31.6 *31.4**	46.5 *19.0**	—	—	89.9 *23.1**
	soil	27.2 *63.0**	51.9 *51.6**	51.8 *21.2**	—	—	130.9 *33.7**
	sum	43.2	100.5	244.7	—	—	388.4
Full maturity stage	biologically reduction N_2	2.1 *6.7**	47.6 *22.8**	75.1 *26.0**	21.5 *26.6**	14.7 *35.6**	161.0 *29.2**
	fertilizer	9.6 *30.7**	70.5 *33.7*	97.1 *33.7**	27.1 *33.5**	12.7 *30.8**	217.0 *31.9**
	soil	19.4 *52.5**	90.9 *43.5**	116.4 *40.3**	32.3 *39.9**	13.9 *33.6**	272.9 *38.9**
	sum	31.1	209.0	288.6	80.9	41.3	650.9
Average total quantity of nitrogen taken up by lupine's individual parts		37.2	154.8	266.7	—	—	—
$LSD_{0.05}$ for total quantity of nitrogen taken up through yellow lupine harvested in flowering and full maturity stage		ns	82.7	ns	—	—	221.0

* Proportional (%) participation in total quantity of nitrogen taken up from all source.

Conclusions

1. The dry matter yield of yellow lupine harvested at full maturity stage was almost twice as high as that at flowering stage. Regardless of the harvest date, leaves and stems made up the largest share in the total yield (about 85 %).

2. Nitrogen content in vegetative parts of lupine was lower at full maturity rather than blooming stage.

3. Share of nitrogen originating from a biological reduction in its total amount uptaken by yellow lupine from different sources was 43.2 % at flowering and 29.2 % at full maturity stage. Quantity of nitrogen from fertilizers and soil made up 23.1 % and 33.7 % of its total amount uptaken by yellow lupine harvested at date I, as well as 31.9 % and 38.9 % collected at date II.

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KUMULACJA BIOLOGICZNIE ZREDUKOWANEGO AZOTU PRZEZ ŁUBIN ŻÓŁTY (*Lupinus luteus*) W RÓŻNYCH JEGO FAZACH ROZWOJOWYCH

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Abstrakt: W doświadczeniu wazonowym określono ilość azotu biologicznie zredukowanego z powietrza przez łubin żółty (*Lupinus luteus)* żyjący w symbiozie z bakteriami *Rhizobium lupini,* zbierany w różnych fazach wzrostu i rozwoju. Największy udział w plonie całkowitym łubinu żółtego zbieranego w fazie kwitnienia stanowiły liście (51,4%), a w fazie dojrzałości pełnej – łodygi (45,7 %). Korzenie tej badanej rośliny stanowiły 14,7 % plonu całkowitego w I terminie zbioru i 6,7 % w II terminie. Plon całkowity łubinu zbieranego w fazie pełnej dojrzałości był prawie dwukrotnie większy niż w fazie kwitnienia. Zawartość azotu ogółem w częściach wegetatywnych łubinu była największa w liściach. Zawartość azotu w korzeniach i łodygach była o około 1/3 mniejsza niż w liściach, natomiast w strączynach i nasionach odpowiednio około dwu- i trzykrotnie większa niż w liściach. Wzbogacenie w azot ^{15}N poszczególnych części gorczycy (rośliny pobierającej azot tylko z nawozu i zapasów glebowych) było większe, w porównaniu z odpowiednimi częściami łubinu (korzystającego dodatkowo z azotu atmosferycznego). Udział azotu pochodzącego z biologicznej redukcji N_2 w całkowitej ilości tego pierwiastka zgromadzonej w korzeniach, łodygach i liściach łubinu zbieranego w fazie kwitnienia stanowił kolejno 9,8, 16,9 i 59,8 % (ogółem w całej roślinie 43,2 %). W fazie dojrzałości pełnej łubinu udział azotu pochodzącego z biologicznej redukcji w całkowitej ilości tego pierwiastka zgromadzonej w korzeniach, łodygach, liściach, strączynach i nasionach stanowił odpowiednio: 6,7; 22,8; 26,0; 26,6 i 35,6 % (ogółem w całej roślinie 29,2 %). W całkowitej ilości azotu pochodzącego ze wszystkich źródeł ilość tego pierwiastka pobrana przez łubin z nawozu stanowiła 23,1 % w fazie kwitnienia i 31,9 % w fazie pełnej dojrzałości, natomiast udział azotu pochodzącego z zapasów glebowych wynosił 33,7 % w I terminie zbioru i 38,9 % w II terminie.

Słowa kluczowe: azot, biologiczna redukcja azotu, łubin żółty, gorczyca biała, izotop ^{15}N

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FOLIAR NITROGEN FERTILISATION AS A FACTOR DETERMINING TECHNOLOGICAL PARAMETERS OF WINTER WHEAT

DOLISTNE NAWOŻENIE AZOTEM JAKO CZYNNIK KSZTAŁTUJĄCY PARAMETRY TECHNOLOGICZNE PSZENICY OZIMEJ

Abstract: Over 2002–2005 at the Experiment Station of the Agricultural University in Nitra, at Sladkovicovo – Novy Dvor, about 30 km away from Nitra (Slovakia) a field experiment was carried out which aimed at defining the effect of different nitrogen fertiliser doses and its application method on the value of selected technological parameters in 'Petrana' winter wheat grain and flour. In the present research a varied nitrogen fertilisation applying the entire dose range resulted in an increase in the content of total protein in 'Petrana' winter wheat grain. However, a significant increase in the value of that character was recorded after the application of 80 kg N · ha^{-1}, as compared with the control and the treatment with 50 kg N · ha^{-1}. A varied nitrogen fertilisation, applying the entire dose range, enhanced the values of the technological parameters studies. However, the nitrogen dose optimal for the key indicators of the baking value of flour, namely the sedimentation index value and bread volume have been defined as 95 kg · ha^{-1} and the content of wet gluten and flour water holding capacity – 80 kg · ha^{-1}.

Keywords: winter wheat, nitrogen fertilisation, technological parameters

The most essential factors which affect wheat yielding and grain quality include mineral fertilisation, especially nitrogen fertilisation [1–10]. It increases the content of total protein in grain and the amount of fractions determining the quantity and quality of gluten which, in turn, has a great effect on the wheat baking parameters. And thus for respective new cultivars, it is indispensable to investigate their reaction to the amount of nitrogen doses, expressed not only in a form of grain yield but also the values of characters defining its quality. Besides the amount of fertiliser doses, similarly the

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application method is of considerable importance since the supply of nitrogen to plants should closely harmonize with their development stages. Over the recent years, more and more often the technology of foliar nitrogen application in a fluid form in wheat has been applied [11–13]. Such a method of applying nitrogen is aimed to increase the effectiveness of fertilisation and to maintain a good quality of the yield.

According to Mazurek and Sulek [14], the yield-forming effect of nitrogen fertilisation depends considerably on the method of fertilisation with this nutrient, however, there is little coverage on the relationship between the application technique and grain quality characters and, as a result, flour.

With that in mind, over 2002–2005 a field experiment was carried out on a medium heavy degraded chernozem the aim of which was to determine the effect of different nitrogen fertiliser doses and its application method on the values of selected technological parameters in 'Petrana' winter wheat grain and flour.

Materials and methods

A field experiment was carried out over 2002–2005 at the Experiment Station of the Agricultural University in Nitra, at Sladkovicovo – Novy dvor (17°34′40″ east longitude and 48°22′20″ west latitude), about 30 km away from Nitra (Slovakia). The research involved 'Petrana' winter wheat grain sown in the amount of 5 m grains $\cdot$ ha^{-1}, exposed to varied nitrogen fertilisation (Dusadam fertiliser – 26 %N). The present research was based on a single-factor field experiment, set up following the randomised blocks method in four replications. The soil (chernozem) reaction was neutral (pH in KCl 6.6). The soil showed mean mineral nitrogen content (N_{min} = 14.0 mg $\cdot$ kg^{-1} soil), mean content of available phosphorus (P = 65.7 mg $\cdot$ kg^{-1} soil), a high content of available potassium (K = 247 mg $\cdot$ kg^{-1} soil), very high content of available calcium (Ca = 331 mg $\cdot$ kg^{-1} soil) and the content of humus of 2.95 %. The plots 10 m^2 (8 × 1.25 m) in size were fertilised with four nitrogen doses: the control without nitrogen (N_0); 50 kg N $\cdot$ ha^{-1} (N_{50}) was applied once at the start of the spring vegetation (into soil); 80 kg N $\cdot$ ha^{-1} (N_{80}) was split: 50 kg N $\cdot$ ha^{-1} was applied at the start of spring vegetation (into soil) and 30 kg N $\cdot$ ha^{-1} was applied at the beginning of the shooting phase (foliar application); 95 kg N $\cdot$ ha^{-1} (N_{95}) was split: 50 kg N $\cdot$ ha^{-1} was applied at the start of spring vegetation (into soil), 30 kg N $\cdot$ ha^{-1} – at the beginning of the shooting phase (foliar application) and 15 kg N $\cdot$ ha^{-1} – after tillering and prior to flowering (foliar application). Spring wheat constituted the forecrop. Tillage, winter wheat sowing and harvest were performed compliant with the agrotechnical requirements optimal for the species. During the experiment, pesticides were used by spraying against viral diseases (prevention treatment: Naztak 10EC at the dose of 0.15 dm^3 $\cdot$ ha^{-1}) and against weeds (Granstar WG75 at the dose of 20 g $\cdot$ ha^{-1}).

In the adequately prepared plant material, the following baking value indices were determined: the falling number (according to Hagberg, PN-ISO-3093) [15], content of total protein (%N $\cdot$ 5.7, PN-75A-04018) [16], content of gluten (PN-A-74-043) [17], sedimentation index value (the Zeleny test, PN-ISO-5529) [18], flour water holding capacity (PN-ISO 5530) [19] as well as bread volume obtained from 100 g of flour (PN-A-74108) [20].

The present research results were statistically verified with the analysis of variance and the boundary differences were estimated using the Tukey test at the significance level of p = 0.05. To define the compounds and relationships between the nitrogen fertilisation applied and the values of the spring wheat quality characters investigated, the results were verified with the analysis of simple correlation.

Weather conditions throughout the experiment (2002–2005 growing seasons) are given in Table 1. Over the 2002/2003 and 2003/2004 growing seasons the mean air temperature were higher and total rainfall lower as compared with many-year means by 0.5 ^{o}C and 0.2 ^{o}C as well as 111.0 mm and 61.7 mm (which accounted for 19.8 % and 9.0 %), respectively. The last experiment year, on the other hand, showed the mean air temperature at the same level as the many-year value, whereas the total rainfall slightly exceeded the mean for years (by 4.2 mm).

Table 1

Weather conditions in the vegetation seasons of 2002–2005

Month	2002/2003		2003/2004		2004/2005		Mean for 30 years	
	Temperature [^{o}C]	Rainfall [mm]	Temperature [^{o}C]	Rainfall [mm]	Temperature [^{o}C]	Rainfall [mm]	Temperature [^{o}C]	Rainfall [mm]
IX	14.9	62.1	15.8	16.0	14.7	35.4	15.4	37.0
X	9.7	78.2	7.9	66.0	11.7	45.3	10.1	41.0
XI	8.0	42.0	7.0	33.0	5.5	45.7	4.9	54.0
XII	–0.5	37.7	0.9	24.0	0.8	26.8	0.5	43.0
I	–1.9	33.0	–3.1	55.9	–0.1	31.0	–1.7	31.0
II	–1.8	0.7	1.6	31.1	–2.7	53.0	0.5	32.0
III	5.1	2.3	4.7	52.8	2.7	3.4	4.7	33.0
IV	10.7	27.0	11.7	36.3	11.0	78.7	10.1	43.0
V	18.8	44.5	14.3	36.9	15.2	60.9	14.8	55.0
VI	21.3	6.5	17.9	93.8	18.0	31.5	18.3	70.0
VII	21.2	92.0	20.0	33.8	20.5	59.0	19.3	64.0
VIII	22.7	24.0	20.1	19.4	19.1	94.5	19.2	58.0
Mean; Total	10.2	450.0	9.9	499.3	9.7	565.2	9.7	561.0

Results and discussion

The winter wheat yield is determined by a number of agrotechnical factors, most importantly nitrogen fertilisation, which coincides with the domestic and international literature reports [2, 5, 6, 21, 22]. The 'Petrana' winter wheat grain yield ranged from 6.68 to 7.59 Mg · ha^{-1}; an average of 7.21 Mg · ha^{-1}.

The falling number is a quality parameter one should start the evaluation of the baking value of grain from since the present results above the norm, namely, 175–200 s (mean activity of α-amylase) can suggest that the present material does not meet the consumption requirements. Sulek et al [12] claim that the falling number value is cultivar-specific and thus it depends on the genotype. The winter wheat grain studied demonstrated the value of the falling number of an average of 345 s (Fig. 1A), which suggests that it can be considered, compliant with the COBORU classification [23], to fall into the group of bread cultivars. The minimum value for that group is 200 s.

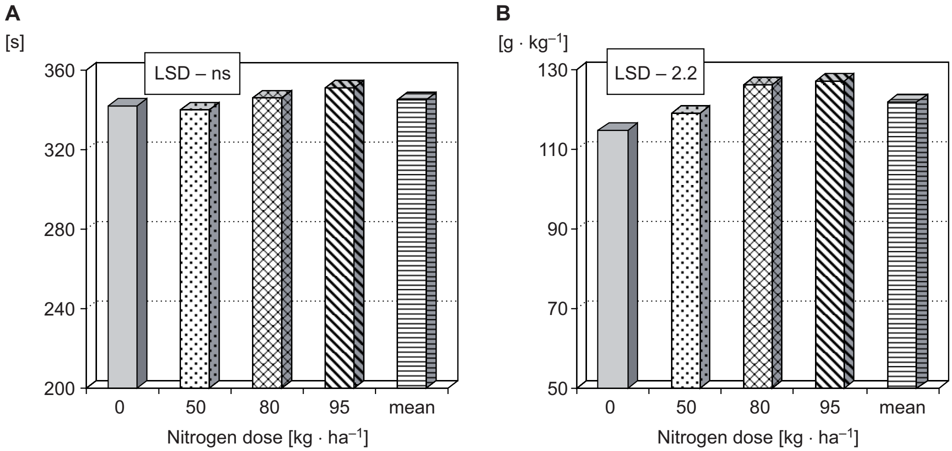

Fig. 1. Mean values of the falling number (A) and the content of total protein (B) in winter wheat grain depending on the nitrogen dose

The present research, similarly as the reports by Budzynski et al [1], Dubis and Borysewicz [2] and Podolska et al [8] showed no significant relationship between the nitrogen dose and the activity of α-amylase, while Knapowski and Ralcewicz [4] indicate that increasing the nitrogen doses under winter wheat to 120 kg · ha^{-1} resulted in a significant increase in the value of the falling number. High nitrogen doses, delaying the vegetation, can thus increase the falling number in the grain of some cultivars [24], and in others – decrease the falling number value [8].

Evaluating baking properties in wheat, much attention is paid to the amount of total protein which is essential not only due to its effect on the nutritious value but also due to the technological properties. The favourable effect of increasing nitrogen fertilisation doses on the content of total protein in wheat grain, in general, coincides with literature reports [1–6, 21, 23, 25] which show that intensifying fertilisation with this nutrient increases the protein content, most often, linearly. In the present research the nitrogen fertilisation level, unlike reported by Lozek and Spychaj-Fabisiak [22], resulted in significant changes in the content of total protein in 'Petrana' winter wheat grain (Fig. 1B). The highest value was noted when nitrogen was applied at the dose of 80 kg · ha^{-1}, when its second part (30 kg) was supplied in a form of foliar fertiliser at the shooting phase, and it was significantly higher than the content of protein in grain from the control and following the application of 50 kg N · ha^{-1}, respectively, by 8.7 % and 5.6 %.

Further increasing of the nitrogen fertilisation dose by 15 kg resulted in an increase in the protein content, however, it was non-significant. Sztuder and Swierczewska [13] report on foliar fertilisers increasing the content of total protein in grain, while Sulek et al [11, 12] demonstrated no significant differences in the content as affected by different nitrogen application methods.

Reports by Budzynski et al [1], Ducsay and Lozek [15] as well as by Lozek and Spychaj-Fabisiak [22] show that winter wheat, irrespective of the nitrogen fertilisation, demonstrated an average content of wet gluten, respectively, of 23.8 %, 28.5 % and 26.5 %. In the present research, the analysis of variance showed that the average content of wet gluten in 'Petrana' winter wheat grain accounted for 29.6 % (Fig. 2A). As reported by Stankowski et al [10], the average value of that character was higher and, depending on the cultivar, ranged from 39.5 % to 42.0 %, while Knapowski and Ralcewicz [3, 5], investigating 'Begra', 'Zyta' and 'Mikon' recorded mean gluten contents: 26.3 %, 30.9 % and 27.5 %, respectively.

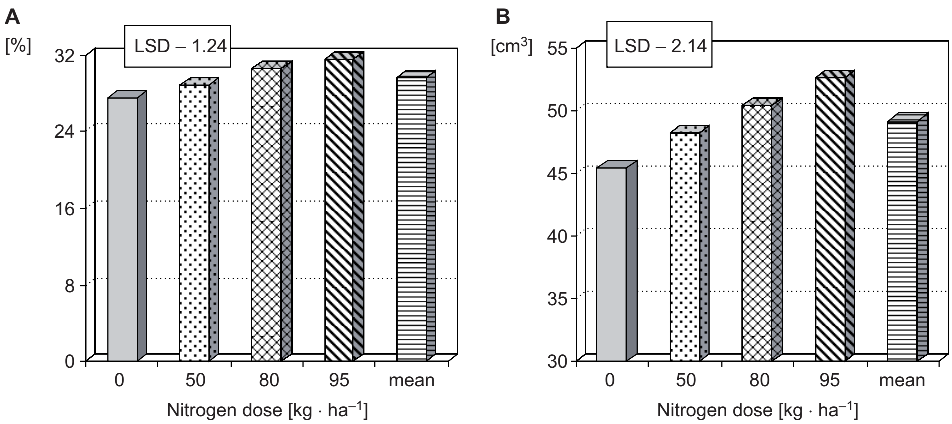

Fig. 2. Mean contents of wet gluten (A) and the values of the sedimentation test (B) in winter wheat grain depending on the nitrogen dose

The higher the nitrogen doses, the higher the content of wet gluten, which is reported by numerous authors [4–9, 10, 21, 22] investigating wheat. As noted by Knapowski and Ralcewicz [3], on average significantly highest amount of wet gluten in wheat grain was recorded after the application of 160 kg N $\cdot$ ha^{-1} (80 + 40 + 40) and it was higher as compared with treatments N_0, N_{80} and $N_{120,}$ by 14.7 %, 9.6 % and 4.7 %, respectively. Budzynski et al [1], on the other hand, investigating winter wheat cultivars, noted the highest significant value of the parameter by applying 180 kg N $\cdot$ ha^{-1}. Sztuder and Swierczewska [13] demonstrated that a clear increase in the amount of wet gluten in grain was due to the application of foliar fertilisers. A combined foliar fertilisation (urea + magnesium sulphate + Polvit Z/J) resulted in a 6.7 % higher content of the parameter, as compared with the control. In the present experiment 'Petrana' winter wheat reacted with a favourable increase in the content of wet gluten to each increase in the nitrogen dose (Fig. 2A), which also coincides with the significantly positive coefficient of simple correlation (r = 0.94) (Table 2). However, one shall assume 80 kg N · ha^{-1} (the other part of the dose – 30 kg as foliar fertiliser at the shooting phase) as the optimal dose. The value recorded for this treatment was significantly higher, as compared with the content of gluten for treatments N_0 and $N_{50,}$ respectively, by 3.1 % and 1.9 %. Sulek et al [11] report on a favourable effect on the value of the above given parameter being attributed to splitting of the nitrogen dose into three parts (the second and the third dose part at the shooting phase and tillering in a fluid form), while Mazurek and Sulek [14] claim that the nitrogen application method does not have a significant effect on the content of gluten.

Table 2

Significant coefficients of simple correlation between the winter wheat characters studied

Parameter		N fertilisation	1	2	3	4	5
Falling number	(1)	ns	—	ns	ns	–0.61	ns
Protein content	(2)	ns	ns	—	ns	ns	ns
Gluten content	(3)	0.94	ns	ns	—	ns	0.94
Sedimentation value	(4)	ns	–0.61	ns	ns	—	ns
Flour water holding capacity	(5)	0.96	ns	ns	0.94	ns	—
Bread volume	(6)	0.84	ns	ns	0.91	0.78	0.81

The analysis of simple correlation identified a close relationship between the content of wet gluten with flour water holding capacity (r = 0.94) and bread volume (r = 0.91) (Table 2). Knapowski and Ralcewicz [3, 5] showed positive relationships between the parameter and the falling number, content of protein, sedimentation index and the bread volume.

On average for the research years a varied nitrogen fertilisation modified the sedimentation index value (Fig. 2B). The higher the nitrogen fertilisation dose, the higher the value of the sedimentation test in flour obtained from winter wheat grain, similarly as in the experiments reported by other authors [1, 2, 4–6, 8]. Its highest (52.7 cm^3) significant value was noted as a result of the nitrogen application of 95 kg · ha^{-1} (50 + 30 + 15) and it was higher than the value for the control, following the application of 50 kg N · ha^{-1} and 80 kg N · ha^{-1} (50 + 30), respectively, by 13.8 %, 8.5 % and 4.4 %. Knapowski and Ralcewicz [4] report on 80 kg N · ha^{-1} to be significant for the sedimentation index value; they demonstrate a positive effect of fertilisation on that character up to 160 kg N · ha^{-1}. Budzynski et al [1], Dubis and Borysewicz [2] as well as Podolska et al [8], on the other hand, identified a favourable effect on the value of that quality character produced by applying nitrogen fertiliser up to, respectively, 150 kg · ha^{-1}, 180 kg · ha^{-1} and 200 kg · ha^{-1}, while Stankowski et al [10] and Spychaj-Fabisiak et al [25] showed that the value of the sedimentation number was not determined by nitrogen fertilisation.

As reported by Budzynski et al [1], flour from the grain of the winter wheat cultivars researched showed a good water holding capacity and accounted for 57.5 %. In the present experiment, in ‘Petrana’ an average value of flour water holding capacity accounted for 58.8 % (Fig. 3A). One shall also note that as for the value of that parameter, based on the classification reported by Podolska and Sulek [23], this cultivar can be considered to represent the elite wheat class (E). Higher mean values of the parameter, as compared with those reported in the present research, were recorded by Podolska et al [8], Stankowski et al [10] and Sulek et al [11] investigating wheat.

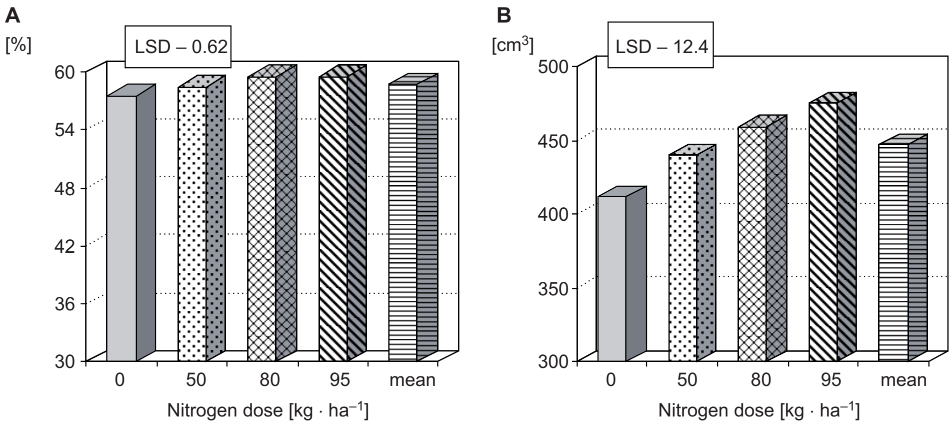

Fig. 3. Mean values of flour water holding capacity (A) and baking volume (B) depending on the nitrogen dose

The effect of the fertiliser factor on that flour character was inconsiderable, however it reached the level of significance, which is confirmed by the analysis of variance and coefficient of simple correlation (r = 0.96; Table 2). The dose of 80 kg N · ha^{-1} turned out to be optimal for flour water holding capacity when its second part (30 kg · ha^{-1}) was applied at the shooting phase (Fig. 3A). As reported by Cacak-Pietrzak et al [26], the highest flour water holding capacity was noted by applying 80 kg N · ha^{-1} (40 kg at the start of vegetation + 40 kg at the shooting phase) for the following cultivars: ‘Almari’, ‘Kobra’ and ‘Panda’. Different results were reported only for ‘Juma’ for which the highest water holding capacity was also recorded for the treatment which involved the dose of 80 kgN · ha^{-1}, however split differently (40 kg at the start of vegetation + 30 kg by spraying at the shooting phase + 10 kg in a form of spray with microelements). Sulek et al [11] report on the highest, although non-significant, value of water holding capacity as a result of the application of 90 kg N · ha^{-1} (the second and third dose part applied in a fluid form at the shooting phase and over tillering). According to Podolska et al [8], increasing the nitrogen fertilisation dose to 120 kg · ha^{-1} resulted in an increase in flour water holding capacity, while further fertilisation increases did not affect that character, whereas Mazurek et al [24] claim that the value of that parameter depended neither on the nitrogen fertilisation dose nor on its application technique.

A direct quality indicator which demonstrates the baking value of wheat grain is the bread volume from test baking. In the present experiment the nitrogen fertilisation applied, similarly as reported in other research with winter wheat [4, 5], increased the

'Petrana' wheat baking volume (Fig. 3B). The highest value of that parameter (475 cm^3) was reported for N_{95} (50 kg at the start of the vegetation, 30 kg at the shooting phase, 15 kg over tillering) and it was significantly higher than the bread volume from the control, N_{50} and N_{80}, respectively, by: 13.3 %, 7.4 % and 3.4 %. Sulek et al [11], investigating the effect of different fertilisation doses and techniques in wheat on its quality parameters, did not observe a significant relationship between the above experimental factors and the bread volume. Similarly Mazurek et al [24] confirmed no effect of the nitrogen application method, however, increasing nitrogen fertilisation from 40 kg to 80 showed significance for that quality character.

Baking volume was significantly positively correlated with the content of gluten (r = 0.91), flour water holding capacity (r = 0.81) and the sedimentation index value (r = 0.78) (Table 2), which supports the claim that an increased share of high-molecule glutenin increases eg the bread volume [27]. Positive relationships of the bread volume with the content of gluten and sedimentation index value were also reported by other authors [4, 5].

Conclusions

1. After the application of the dose of 80 kg $N \cdot ha^{-1}$ there were noted significantly higher contents of total protein and wet gluten in grain as well as flour water holding capacity of the winter wheat cultivar investigated than the corresponding values determined after the nitrogen application at the dose of 50 $kg \cdot ha^{-1}$ and when compared with the control.

2. Varied nitrogen fertilisation, for the entire dose range applied, significantly determined mean sedimentation index values and bread volume in 'Petrana' winter wheat.

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DOLISTNE NAWOŻENIE AZOTEM JAKO CZYNNIK KSZTAŁTUJĄCY PARAMETRY TECHNOLOGICZNE PSZENICY OZIMEJ

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Abstrakt: W latach 2002–2005 w Zakładzie Doświadczalnym Uniwersytetu Rolniczego w Nitrze, w miejscowości Sládkovičovo – Nový Dvor, około 30 km od Nitry (Słowacja) przeprowadzono doświadczenie polowe, którego celem było określenie wpływu różnych dawek nawożenia azotem i sposobu jego aplikacji na wartość wybranych parametrów technologicznych w ziarnie i mące pszenicy ozimej odmiany Petrana. W przeprowadzonych badaniach zróżnicowane nawożenie azotem w całym zakresie stosowanych dawek powodowało wzrost zawartości białka ogólnego w ziarnie pszenicy ozimej odmiany Petrana. Jednak udowodniony statystycznie przyrost wartości badanej cechy uzyskano po zastosowaniu 80 kg N $\cdot$ ha^{-1} w stosunku do obiektu kontrolnego i obiektu, gdzie zastosowano 50 kg N $\cdot$ ha^{-1}. Zróżnicowane nawożenie azotem, w całym zakresie stosowanych dawek, powodowało korzystny wpływ na wartości badanych parametrów technologicznych. Jednak za optymalne dawki azotu dla najważniejszych wyróżników wartości wypiekowej, tj. wskaźnika sedymentacji i objętości pieczywa przyjęto 95 kg $\cdot$ ha^{-1} oraz zawartości mokrego glutenu i wodochłonności mąki – 80 kg $\cdot$ ha^{-1}.

Słowa kluczowe: pszenica ozima, nawożenie azotem, parametry technologiczne

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CONTENT OF TOTAL NITROGEN AND ITS MINERAL FORMS IN SOIL AFTER THE APPLICATION OF A VARIED SULPHUR FERTILISATION

ZAWARTOŚCI AZOTU OGÓŁEM I JEGO FORM MINERALNYCH W GLEBIE PO ZASTOSOWANIU ZRÓŻNICOWANEGO NAWOŻENIA SIARKĄ

Abstract: Over years 2005–2007 research was carried out to determine the effect of sulphur fertilisation on the content of total nitrogen and its mineral forms in Luvisol. Sulphur was applied in an ionic form as sodium sulphate(VI) and in an elemental form as Siarkol Extra at the dose: 0, 20, 40, 60 kg per hectare. Following the application of sulphur at the dose of 60 S kg · ha^{-1}. A significant increase was recorded in the mean content of total nitrogen in soil, as compared with the control. There was shown no clear effect of neither the sulphur form applied nor its dose on the mean content of ammonium nitrogen in soil, while those factors significantly differentiated the content of nitrate nitrogen(V) in soil.

Keywords: sulphur, fertilisation, total nitrogen, mineral nitrogen forms

Over the recent years the transformation of economy and proecological actions have resulted in an about 40 % decrease in sulphur dioxide emissions in Poland. There has been a limited supply of sulphur from industrial emissions, which decreased the content of this macronutrient in soil considerably, thus decreasing the value of ratio N:S in plants, being an essential yield quality indicator [1, 2]. Today in Poland more than half of the soils used for agricultural purposes demonstrates natural or low sulphur content [3]. This element participates in plant metabolic processes, is a building component of proteins and an essential part of exogenous amino acids and thus constitutes an indispensable component of living organisms [4, 5].

With that in mind, research has been launched to determine the effect different forms of sulphur and the dose on the content of total nitrogen and its mineral forms in Luvisol.

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Material and methods

The research involved soil sampled from a two-factor static field experiment set up following the randomized complete block design, at the Experiment Station of the Faculty of Agriculture at Wierzchucinek in the vicinity of Bydgoszcz. The research was performed over years 2005–2007 based on three parallel field experiments carried out in three repetitions. The experiments involved the following crops:

Experiment I: 2005 – spring barley, 2006 – narrow leaf lupin, 2007 – mustard.

Experiment II: 2005 – narrow-leaf lupin, 2006 – mustard, 2007 – spring barley.

Experiment III: 2005 – mustard, 2006 – spring barley, 2007 – narrow-leaf lupin.

The experiment was carried out in Haplic Luvisol, of good rye complex. In the year in which the experiment was established the soil demonstrated the following properties: pH_{KCl} – 5.8; humus content 1.13 %; total nitrogen content – 0.72 $g \cdot kg^{-1}$; ratio C:N – 8.9:1.

The factors investigated were the sulphur forms (n = 2, factor I) and doses (n = 4, factor II) of sulphur-containing compounds. They were used in an ionic form as sodium sulphate(VI) and as elemental sulphur in a form of Siarkol Extra, at the following doses in kilograms per hectare: 0, 20, 40, 60. Sulphur fertilisers were applied into soil, once prior to plant sowing. After three research years the soil was sampled from the arable layer (0–25 cm); the following were determined in the samples: total nitrogen with the Kjeldahl method, ammonium nitrogen with the distillation method and nitrate(V) nitrogen colorimetrically with phenoldisulphonic acid.

The results were statistically verified, applying the analysis of variance; the differences were verified with the Tukey test at the significance level of $\alpha = 0.05$.

Results and discussion

After the application of sulphur at the dose of 60 $kg\ S \cdot ha^{-1}$ there was noted a significant increase (by 1.4 %) in the mean content of total nitrogen in soil as compared with the control. The other sulphur doses investigated (20 $kg \cdot ha^{-1}$ and 40 $kg \cdot ha^{-1}$) did not differentiate the mean content of total nitrogen in soil significantly (Table 1). Similarly Klikocka [6] did not observe significant changes in the content of total nitrogen in soil following the application of different sulphur doses (25 and 50 kg $S \cdot ha^{-1}$) in a form of ammonium sulphate(VI) when growing triticale. One shall note that the highest dose (60 $kg\ S \cdot ha^{-1}$) applied for lupin growing was the only one which resulted in a significant increase in the mean content of total nitrogen in soil as compared with the treatments with the fertilisation dose of 40 $kg\ S \cdot ha^{-1}$. After three research years it was observed that the varied sulphur dose affected the nitrogen concentration in soil neither under spring barley nor under mustard. Interestingly, of all the sulphur doses applied, the dose of 20 $kg\ S \cdot ha^{-1}$ in a form of sodium sulphate(VI) was the only one which demonstrated a clearly more favourable effect on the content of total nitrogen than the same amount of sulphur contained in a form of Siarkol Extra.

Table 1

Content of total nitrogen in soil [N g · kg^{-1}]

Experiment	Form of sulphur	Sulphur dose [kg S · ha^{-1}]				Mean	$LSD_{0.05}$
		0	20	40	60		
I	Na_2SO_4	0.71	0.74	0.72	0.73	**0.72**	I – ns II – ns I in II – ns II in I – ns
	Siarkol*	0.73	0.71	0.73	0.74	**0.73**	
	Mean	**0.72**	**0.72**	**0.72**	**0.73**	**0.72**	
II	Na_2SO_4	0.62	0.67	0.67	0.63	**0.65**	I – ns II – ns I in II–0.049 II in I – 0.068
	Siarkol*	0.60	0.60	0.64	0.66	**0.62**	
	Mean	**0.61**	**0.63**	**0.65**	**0.64**	**0.63**	
III	Na_2SO_4	0.78	0.78	0.74	0.77	**0.76**	I – ns II – 0.030 I in II – 0.039 II in I – 0.042
	Siarkol*	0.75	0.73	0.73	0.77	**0.74**	
	Mean	**0.76**	**0.75**	**0.73**	**0.77**	**0.75**	
Mean	Na_2SO_4	0.70	0.73	0.71	0.71	**0.71**	I – ns II – 0.001 I in II – 0.026 II in I – 0.002
	Siarkol*	0.69	0.68	0.70	0.72	**0.70**	
	Mean	**0.70**	**0.70**	**0.70**	**0.71**	**0.70**	

* Siarkol – elemental sulphur.

As reported in literature [7], the excessive amount of sulphur introduced into soil both in a form of acid rain or dry deposition affects the soil processes thus decreasing eg the amount of cations Ca^{2+} and Mg^{2+}. As a result, the soil gets poorer in alkaline components. The soil researched showed a slightly acidic reaction, however, the application of sulphur at the doses and forms compliant with the assumptions of the experiment did not result in considerable changes in the content of total nitrogen.

Mineral nitrogen forms are most easily available for plants and their contents in soil are used to define nitrogen doses and they are an indicator of the soil environment status [8].

Mean contents of ammonium nitrogen, as affected by the experimental factors investigated, varied and reached in soil under mustard (experiment I), spring barley (experiment II), yellow lupin (experiment III), respectively: 13.8 mg · kg^{-1}, 13.4 mg · kg^{-1} and 16.2 mg · kg^{-1}.

Under the conditions of the present experiment, there was demonstrated no clear effect of neither the sulphur form applied nor its dose on the content of ammonium nitrogen in soil (Table 2). One shall, however, note that as a result of the sulphur doses applied, the contents of this nitrogen form slightly decreased, as compared with the control, reaching the lowest value equal to 16 mg · kg^{-1} after the use of 60 kg S · ha^{-1}. According to Kopec [4], a combined mineral fertilization (NPK) increases the nitrogen leaching considerably. Reports by Spychaj-Fabisiak and Murawska [10] confirm that ammonium nitrogen is especially heavily leached from acid soil, and one shall stress that the experiment was carried out on slightly acidic soil. The intensity of leaching also effected the mineral nitrogen dose, soil type and the amount and reaction of precipitation [11]. However, in the present research there was noted a more favourable effect of Siarkol Extra thanks to which in each fertilisation treatment the mean content of ammonium nitrogen was significantly higher as compared with the treatments with sodium sulphate(VI) fertiliser. Siarkol Extra gets solved in water much harder, and so its acidifying effect is lower, which, in turn, could have led to lower ammonium nitrogen leaching. It was also demonstrated that the experimental factors did not differentiate the mean content of this nitrogen form determined in soil after harvest of mustard, spring barley and lupin.

Table 2

Content of ammonium nitrogen in soil [$N\text{-}NH_4^+$ mg · kg^{-1}]

Experiment	Form of sulphur	Dose of sulphur [kg S · ha^{-1}]				Mean	$LSD_{0.05}$
		0	20	40	60		
I	Na_2SO_4	14.4	13.5	12.6	12.2	**13.2**	I – ns II – ns I in II – ns II in I – ns
	Siarkol*	15.4	14.0	14.0	13.8	**14.3**	
	Mean	**14.9**	**13.8**	**13.3**	**13.0**	**13.7**	
II	Na_2SO_4	12.6	13.1	12.6	12.2	**12.6**	I – 1.398 II – ns I in II – 1.533 II in I – 0.739
	Siarkol*	14.0	13.6	14.6	14.4	**14.2**	
	Mean	**13.3**	**13.4**	**13.6**	**13.3**	**13.4**	
III	Na_2SO_4	20.6	21.4	21.0	21.3	**21.0**	I – ns II – 0.667 I in II – ns II in I – ns
	Siarkol*	21.8	22.4	22.4	22.0	**22.2**	
	Mean	**21.2**	**21.9**	**21.7**	**21.7**	**21.6**	
Mean	Na_2SO_4	15.5	16.0	15.4	15.2	**15.5**	I – 0.440 II – 0.278 I in II – 0.454 II in I – 0.393
	Siarkol*	17.4	16.7	17.0	16.7	**17.0**	
	Mean	**16.5**	**16.3**	**16.2**	**16.0**	**16.2**	

* Siarkol – elemental sulphur.

Nitrate(V) nitrogen is a form totally soluble in water. It shows a special mobility, does not undergo physicochemical sorption, which makes it easily leaching deep down the profile, thus contaminating ground and surface waters [12].

The content of nitrate(V) nitrogen in soil (Table 3) depended significantly on the experimental factors. The total mean content of this nitrogen form was 3.46 mg · kg^{-1}. On average the highest content of nitrate(V) nitrogen was recorded in the soil under mustard (5.98 mg · kg^{-1}), while the lowest – soil under narrow-leaf lupin – 1.82 mg · kg^{-1}. On average the highest content of nitrate(V) nitrogen was recorded for soil under mustard (5.98 mg · kg^{-1}), whereas the lowest – the soil under narrow-leaf lupin – 1.82 mg · kg^{-1}. However, due to Siarkol Extra fertilization, the content of nitrate(V) nitrogen in soil was on average 3.57 mg · kg^{-1} and it was 6.6 % significantly higher than the one recorded due to the application of sodium sulphate(VI). There was also observed a significant increase in the mean content of this nitrogen form due to different sulphur doses. This increase, as compared with the control, was highest after the application of 60 kg S · ha^{-1} and it accounted for 2.9 %.

Table 3

Content of nitrate nitrogen (V) in soil [N-NO_3^- mg · kg^{-1}]

Experiment	Form of sulphur	Dose of sulphur [kg S · ha^{-1}]				Mean	$LSD_{0.05}$
		0	20	40	60		
I	Na_2SO_4	5.21	5.39	5.21	6.53	**5.58**	I – 0.294 II – 0.249 I in II – 0.384 II in I – 0.352
	Siarkol*	5.52	5.85	6.33	7.86	**6.39**	
	Mean	**5.36**	**5.62**	**5.77**	**7.19**	**5.98**	
II	Na_2SO_4	3.12	3.27	2.58	2.36	**2.83**	I – 0.046 II – 0.315 I in II – ns II in I – ns
	Siarkol*	3.13	3.32	2.50	2.70	**2.91**	
	Mean	**3.13**	**3.29**	**2.54**	**2.53**	**2.87**	
III	Na_2SO_4	1.74	1.69	1.72	1.82	**1.74**	I – ns II – 0.103 I in II – 0.159 II in I – 0.146
	Siarkol*	2.05	1.65	1.85	2.07	**1.90**	
	Mean	**1.89**	**1.67**	**1.78**	**1.94**	**1.82**	
Mean	Na_2SO_4	3.35	3.30	3.17	3.57	**3.35**	I – 0.076 II – 0.034 I in II – 0.048 II in I – 0.070
	Siarkol*	3.57	3.61	3.56	3.54	**3.57**	
	Mean	**3.46**	**3.45**	**3.36**	**3.56**	**3.46**	

* Siarkol – elemental sulphur.

One shall note that the experimental factors studied clearly differentiated the content of nitrate(V) nitrogen in soil under spring barley. There was recorded a more favourable effect of Siarkol Extra after the application of which a 2.8 % increase in the content of nitrate(V) nitrogen in soil was identified as compared with the treatments with sodium sulphate(VI) fertiliser. Following the application of the highest sulphur doses investigated (40 kg S · ha^{-1} and 60 kg S · ha^{-1}), there was a clear decrease in the content of nitrate(V) nitrogen in soil which was, respectively: 18.8 % and 19.2 %, as compared with the control.

In the soil under narrow-leaf lupin, after the application of the dose of 20 kg S · ha^{-1} there was recorded a significant decrease, as compared with the control, in the content of nitrate(V) nitrogen (by 11.6 %). However, there was recorded no clear effect of the kind of the sulphur fertiliser on the content of this form of nitrogen.

Conclusions

1. After the application of sulphur at the dose of 60 kg S · ha^{-1} there was recorded a significant increase in the content of total nitrogen in soil, as compared with the control.

2. The content of nitrate(V) nitrogen in the soil researched depended significantly both on the sulphur form and its dose, however in the case of ammonia nitrogen no such relationship was recorded.

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ZAWARTOŚCI AZOTU OGÓŁEM I JEGO FORM MINERALNYCH W GLEBIE PO ZASTOSOWANIU ZRÓŻNICOWANEGO NAWOŻENIA SIARKĄ

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Abstrakt: W latach 2005–2007 przeprowadzono badania, których celem było określenie wpływu nawożenia siarką na zawartość azotu ogółem i jego form mineralnych w glebie płowej. Siarkę stosowano w postaci jonowej w formie siarczanu(VI) sodu oraz w postaci elementarnej jako Siarkol Extra w dawkach: 0, 20, 40, 60 kg na hektar. Po zastosowaniu siarki w dawce 60 S kg $\cdot$ ha^{-1} stwierdzono znaczny wzrost średniej zawartości azotu ogółem w glebie, w porównaniu do obiektu kontrolnego. Nie wykazano wyraźnego wpływu zastosowanej formy siarki, jak również jej dawki na średnią zawartość azotu amonowego w glebie, natomiast czynniki te w znaczny sposób różnicowały zawartości azotu azotanowego(V) w glebie.

Słowa kluczowe: siarka, nawożenie, azot ogółem, mineralne formy azotu

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EFFECT OF MUNICIPAL WASTES MOISTURE LEVEL ON TRANSFORMATIONS OF NITROGEN FORMS IN THE COURSE OF COMPOSTING

WPŁYW UWILGOTNIENIA ODPADÓW KOMUNALNYCH NA PRZEMIANY FORM AZOTU W CZASIE KOMPOSTOWANIA

Abstract: The aim of the study was to determine the influence of municipal wastes moisture level of on the intensity of transformations of various forms of nitrogen during composting. The object of the study was fresh (heating) compost leaving the technological line of the composting plant MUT-DANO in Katowice. Composting of that material was conducted for a period of 5 months under the following conditions: variant A – pile on plastic foil, with moisture content of 0.5 kg H_2O kg^{-1} dm, variant B – perforated plastic container of ca 1 m^3 in capacity, with moisture content of 0.5 kg H_2O kg^{-1} dm, variant C – perforated plastic container of 1 m^3 in capacity, with moisture content of 0.6 kg H_2O kg^{-1} dm. The composted material was stirred at intervals of 10–15 days for aeration, moisture content of the material was determined, water deficit was replenished, and samples were taken for laboratory analyses. In collected samples the following determinations were performed: humidity, ash content, contents of different nitrogen forms: N_t – total nitrogen, N_w – water-soluble nitrogen (1:10), N-NH_4^+ and N-NO_3^- – mineral nitrogen in water extract, $N_{w\ org.}$ – organic nitrogen in water extract. Based on this results the total nitrogen losses were calculated. Obtained results shows that moisture of composted municipal wastes plays an important role in the shaping of the fertility properties of composts and determines the content of total N and the transformation of its organic and mineral forms. Composting of municipal wastes on the pile, accelerated the maturation of composts and was conducive to the obtainment of product richer in nitrogen, with a higher content of N-NO_3^-. Also higher moisture content of composted municipal wastes did not ensure their sufficient oxygenation, which led to greater losses of nitrogen, reduced the quality of compost, and did not ensure sanitary safety. Higher moisture content limited and modified the rate of biochemical transformations in composted municipal wastes.

Keywords: composting of municipal wastes, nitrogen transformation, moisture level

Low contents of nitrogen in mineral soils, at high requirements for proper growth of plants, indicate the need for supplementation of that component through application of

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mineral or organic fertilizers. Energy-consuming and costly production of nitrogen fertilizers makes it a necessity to search for cheaper nitrogen sources that may be organic waste materials. Such materials include, among other things, municipal wastes that so far are mostly kept at wastes dump [1]. Municipal solid wastes (MSW), collected selectively, contain notable amounts of organic mater and of macro- and micro-components. In view of the data given by Baran and Turski [1], the content of nitrogen in municipal wastes in Poland varies within the broad range of 3–30 g kg^{-1}.

Composting of municipal wastes permits recycling of organic and mineral components contained in them. This manner of utilization of wastes allows the creation of a valuable material that can be used for improvement of the properties of soil environment.

In the light of earlier studies by Drozd et al [9], it appears that composts produced of non-segregated municipal wastes of the agglomeration of Katowice contained nitrogen at the level of 10.9–13.0 g kg^{-1}. Composts produced from sorted municipal wastes are richer in total nitrogen (10–24 g kg^{-1}) [10, 19]. The processes of transformation of organic matter depend on the properties of the initial material and on the conditions of composting [2, 7, 8, 15, 17, 18]. Apart from the C/N ratio, another significant factor for correct composting is moisture content and oxygenation. These conditions determine the duration and intensity of the particular phases of composting, ensure biological and biochemical transformations of organic matter, and sanitary safety of composts. Temperature and duration of phases of composting play an important role in nitrogen transformations that include the processes of ammonification, nitrification and de-nitrification.

A consequence of composting conditions are losses of nitrogen caused by emission of NH_3, nitrogen oxides and N_2, determining the level of total nitrogen content N_t and the value of the C/N ratio [6, 14, 18].

Literature of the subject provides reports on a wide range of moisture levels (45–70 %) applied during composting [15, 17, 18]. In Poland, maturation of fresh composts produced from municipal wastes is most frequently conducted on piles, with periodic aeration and wetting, without considering the effect of those measures on the quality of the end product.

The aim of the study was to determine the influence of municipal wastes moisture level on the intensity of transformations of various forms of nitrogen during composting.

Material and methods

The object of the study was fresh (heating) compost leaving the technological line of the composting plant MUT-DANO in Katowice. Composting of that material was conducted for a period of 5 months under the following conditions:

– variant A – pile on plastic foil, with moisture content of 0.5 kg H_2O kg^{-1} dm on the day of aeration, with variation of 0.44–0.524 kg kg^{-1},

– variant B – perforated plastic container of ca 1 m^3 in capacity, with moisture content of 0.5 kg H_2O kg^{-1} dm on the day of aeration, with variations of 0.462–0.534 kg kg^{-1},

– variant C – perforated plastic container of 1 m^3 in capacity, with moisture content of 0.6 kg H_2O kg^{-1} dm on the day of aeration, with variation of 0.469–0.6 kg kg^{-1}.

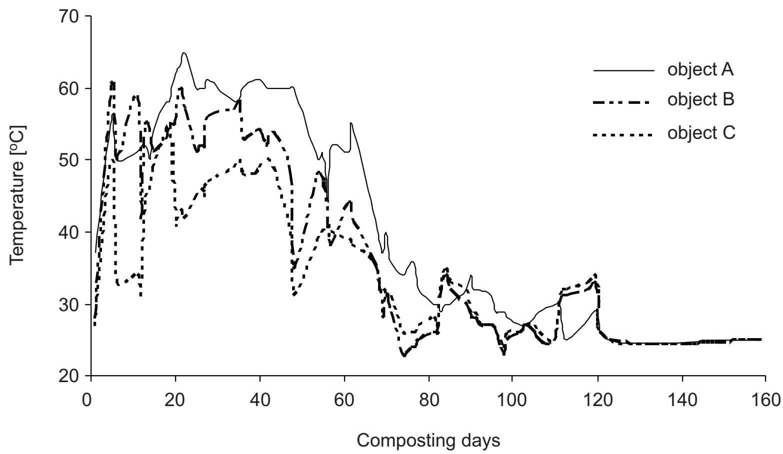

Fig. 1. Changes of the temperature during composting

The composted material was stirred at intervals of 10–15 days for aeration, moisture content of the material was determined, water deficit was replenished, and samples were taken for laboratory analyses, point-wise from 20 points, and mixed together to create averaged samples. In the course of the experiment, temperature of composted material was measured at intervals of 2–3 days (Fig. 1). Samples taken at various times of composting (after 11, 22, 36, 54, 68, 82, 95, 112, 126, 143 and 159 days) were used for the following determinations:

– moisture content – with the oven-dry method,

– ash content after combusting a weighed portion in an oven at temperature of 550 °C,

– N_t and N_w – total nitrogen and water-soluble nitrogen (1:10), with the Kjeldahl method,

– $N\text{-}NH_4^+$ and $N\text{-}NO_3^-$ – in water extract, using Braun Luebbe analyser,

– $N_{w\ org.}$ – organic nitrogen in water extract, from the difference of $N_w - (N\text{-}NH_4^+ + N\text{-}NO_3^-)$.

Results presented in this paper are average from two repeats.

Based on the obtained results, calculations were made of losses in total nitrogen content, on the basis of the initial (X_1) and final (X_2) levels of ash and initial (N_{t1}) and final (N_{t2}) nitrogen contents according to the formula: N_{losses} (%) = $100 - 100(X_1 \cdot N_{t2})/(X_2 \cdot N_{t1})$ [4]. Obtained results were statistically verified at significance level $\alpha = 0.05$.

Results

The study showed that moisture played an important role in shaping the values of total nitrogen content N_t and of the content of its soluble forms in the particular phases of composting (Figs. 2–6). In the course of composting there was an increase in the total nitrogen content N_t in all the experimental variants. Composts maturing on the pile (variant A) displayed, over the whole period of composting, a gradual increase of N_t and, at the same time, a lower content of total nitrogen compared with the other experimental objects. Likewise, in the maturation of composts with moisture content of

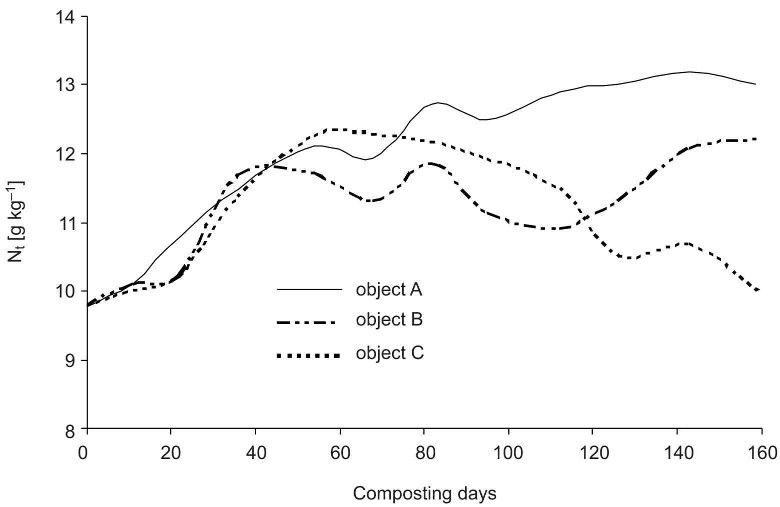

Fig. 2. Changes of total nitrogen (N_t) contents during composting

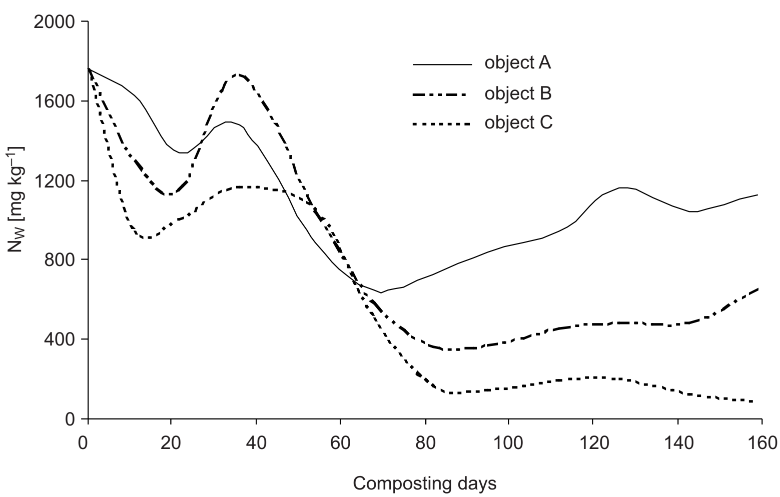

Fig. 3. Changes of water – soluble nitrogen (N_w) contents during composting

0.5 kg H_2O kg^{-1} dm (variant B), the content of N_t increased, and its level after 159 days was higher by ca 2.5 g kg^{-1} dm in comparison with the initial material. The application of higher moisture level in the experiment (0.6 kg H_2O kg^{-1} dm, variant C) was not conducive to the formation of compost rich in nitrogen. In the analysed variant C, increase in the level of nitrogen continued until day 68 (Fig. 2), and subsequently its content gradually decreased and on day 159 of composting was higher by 0.24 g kg^{-1} dm than in the initial material. These data indicate that in the process of composting at moisture level of 0.6 kg H_2O kg^{-1} dm there occurred, in the final phase, considerable losses of nitrogen. This finds support in the level of water-soluble forms of nitrogen and in the calculated losses of N_t (Fig. 3–7). During the composting, in all the experimental variants the level of water-soluble forms of nitrogen (N_w) displayed a general decreasing trend, with observable variations. In the mesophilic phase, around days 20–25 of composting, there occurred the first rapid drop in the content of water-soluble forms N_w, most pronounced in variant C, and the least in variant A. In the thermophilic phase, around days 35–40 of composting, a notable increase was observed in the level of N_w, followed by a strong decrease. The lowest (642 mg kg^{-1}) were recorded on day 68 in treatment A, in treatment B on day 82 (359 mg kg^{-1}) and in treatment C on day 95 of composting (142 mg kg^{-1}). In subsequent periods of maturation of the composts the content of water-soluble forms of nitrogen increased again. The increase was more intense in composts maturing on the pile, somewhat slower at moisture level of 0.5 kg H_2O kg^{-1} dm (variant B), and only slight at moisture level of 0.6 kg H_2O kg^{-1} dm. This differentiation in the content of water-soluble forms of nitrogen and their level after 159 days of composting indicate that the higher level of moisture in the composted material inhibited the rate of oxygen transformations of nitrogen. This is supported by the contents of water-soluble forms: $N_{w\ org.}$, N-NH_4^+ and N-NO_3^- (Fig. 4–6).

The level of water-soluble organic nitrogen ($N_{w\ org.}$) decreased in the process of maturation of the composts (Fig. 6). This was observable especially in the mesophilic

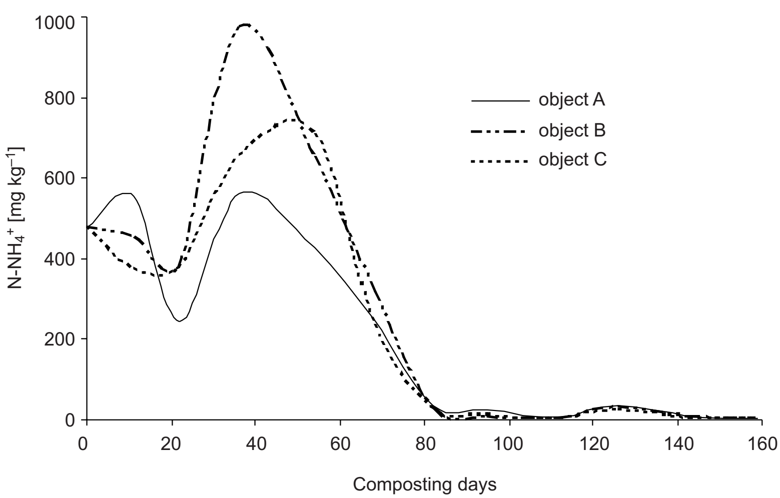

Fig. 4. Changes of N-NH_4^+ contents during composting

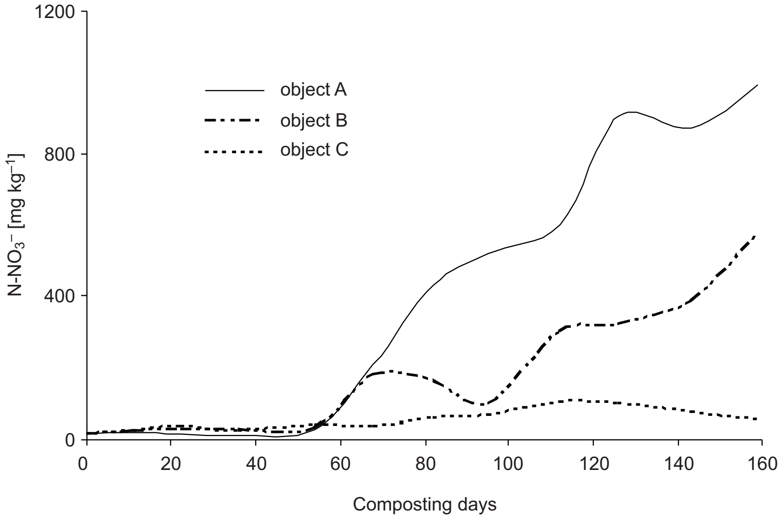

Fig. 5. Changes of $N\text{-}NO_3^-$ contents during composting

and thermophilic phases of composting. A slightly higher content of water-soluble forms of organic nitrogen was found in the compost maturing on the pile, remaining under somewhat more favorable oxygenation conditions. The lowest level of that form of nitrogen was found at moisture content of 0.6 kg H_2O kg^{-1} dm (variant C).

The amounts of $N\text{-}NH_4^+$ and $N\text{-}NO_3^-$ indicate that the processes of ammonification take place at a higher rate in the thermophilic phase of composting, and those of nitrification in the phase of cooling and maturity of composts (Fig. 4–5). Composting conditions affected on $N\text{-}NH_4^+$ content in thermophilic composting phase. Notably

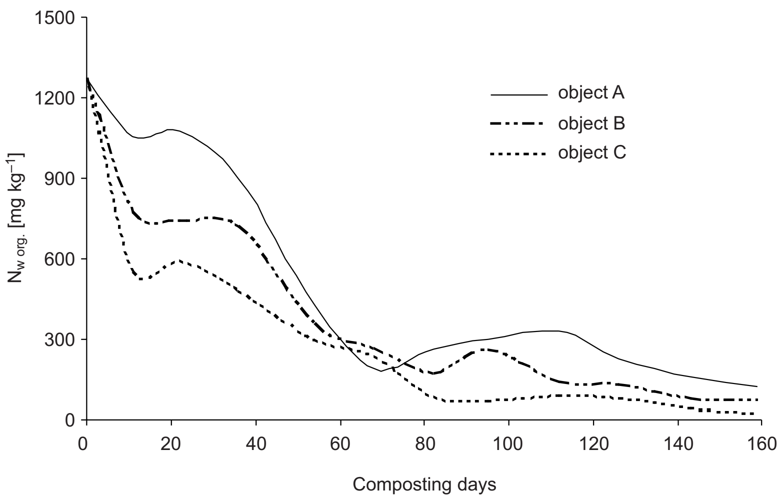

Fig. 6. Changes of $N_{w\ org}$ contents during composting

greater levels of $N\text{-}NH_4^+$ was recorded in composts maturing at the moisture contents of 0.5 kg H_2O kg^{-1} dm (variant B) and 0.6 kg H_2O kg^{-1} dm (variant C), than on the pile. In the phase of cooling, the content of $N\text{-}NH_4^+$ decreased rapidly in all the treatments.

On day 82 of composting it was only 5–7 %, and in mature composts did not exceed 1 % of the initial levels.

The composting conditions determined also the content of $N\text{-}NO_3^-$ in the course of the composting process. Very low and similar levels of that form on nitrogen were observed in water extracts from all the treatments in the mesophilic and thermophilic phases of composting. In the cooling and maturation phases the level of that form of nitrogen increased rapidly in composts maturing on the pile, more slowly in the container at moisture content of 0.5 kg H_2O kg^{-1} dm, and only slightly in variant C, at moisture level of 0.6 kg H_2O kg^{-1} dm.

The above analysis indicates that moisture level of composted mass and its oxygenation play an important role in the process of maturation of composts and determine their fertilizer value, expressed in the content of total nitrogen and its mineral forms.

In the light of the results obtained, the content of total nitrogen N_t in mature composts is determined mainly by the level of losses that were notably higher in composting at the higher moisture content (Fig. 7).

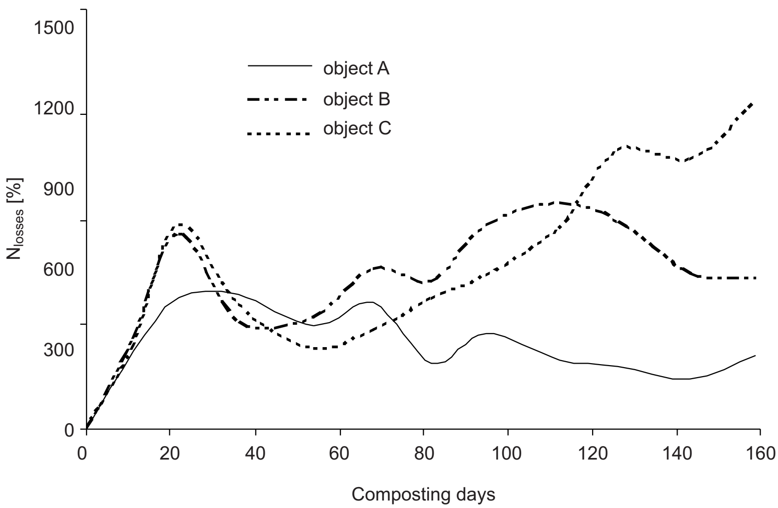

Fig. 7. Losses of nitrogen ($N_{loss.}$) during composting

Losses of total nitrogen took place over the whole period of composting, at various rates. In composts maturing on the pile (treatment A) they were observed mainly in the thermophilic phase of composting. However, quantitatively the greatest losses of nitrogen in composting were recorded at the moisture level of 0.6 kg H_2O kg^{-1} dm. Intensive losses of N in that treatment took place between days 11 and 36 in the thermophilic phase of composting, and very intensive – in further phase of composting.

These data indicate that nitrogen losses in the course of composting could have been caused by nitrogen volatilization in the form of ammonia in the thermophilic phase of composting, and in other gaseous forms in the process of nitrification, in the cooling phase.

Discussion

Composting, commonly defined as a process of bio-oxidation of heterogeneous organic matter, is an effect of living dynamic succession of microorganisms [3]. In the process of composting, deep transformations take place in organic matter and in mineral compounds, including nitrogen. The aim of composting is the obtainment of fertilisers with high effectiveness and rich in nitrogen, among other things. Composting conditions have a significant effect on transformation of nitrogen, presence of water-soluble forms, nitrogen losses, and its content in the end product.

In literature [6, 12, 14] it is emphasized that nitrogen losses are determined by temperature, pH and quality of composted material. They are low when composting wastes rich in lignincelluloses, and increase under interaction of higher temperature and pH in the thermophilic phase of composting. In the experiment presented here, the run of temperatures in the process of composting had an effect on the rate of nitrogen transformations and on the level of its losses. The more favorable aeration conditions in the pile, at moisture level of 0.5 kg H_2O kg^{-1} dm, were conducive to intensive growth of thermophilic bacteria, which led to increase in temperature of the composted material.

The temperature in the pile in the initial two weeks of composting was within the range of 37–56 ^oC (Fig. 1), most frequently assuming values around 50 ^oC, and in the thermophilic phase increased to 60–65 ^oC. In the light of data reported by Pragans et al [12], such a run of temperatures in the thermophilic phase of composting ensures sanitation of composts, at the same time reducing the level of nitrogen losses in the form of ammonia. The above supposition finds confirmation in the intensive increase of N_t and $N_{w\ org.}$ in comparison with the other variants. At the same time, the higher rate of decrease in the content of $N\text{-}NH_4^+$ indicates its rapid immobilisation by microorganisms and its incorporation into structures of specific humus compounds [8].

In the subsequent phases of maturation of composts on the pile the losses of nitrogen decreased (Fig. 7), and its total content slowly increased (Fig. 2). On day 159 of maturing on the pile, the compost was characterised by the highest content of N_t compared with the other variants. This resulted, among other things, from low losses of nitrogen than on day 159 amounted to ca 7 % at LSD only 0.7.

In the analyzed period, the content of $N\text{-}NH_4^+$ in water extracts decreased, and that of $N\text{-}NO_3^-$ increased, and intensive processes of nitrification took place especially when the temperature dropped below 40 ^oC [14].

The more favorable composting conditions on the pile, at moisture level of 0.5 kg H_2O kg^1 dm, determined also faster maturation process of the compost. It is accepted after Pare et al [11] that the ratio of $N\text{-}NH_4^+/N\text{-}NO_3^-$ informs about the intensity of processes of biological decomposition. Its value below 0.16 is, according to Bernal et al [5] one of the indicators of compost maturity. On this basis we can assume that the compost produced on the pile reached maturity after 82 days of composting.

Whereas, at the moisture level of 0.5 kg H_2O kg^{-1} dm (variant B), already in the first week of composting the temperature exceeded 55 °C. This caused increase in the level of nitrogen losses that, throughout the whole period of composting, were at a higher level than on the pile. The effect of this was a reduction in the content of N_t in the final product. Among the mineral forms of nitrogen, in the thermophilic phase of composting the content of N-NH_4^+ increased nearly twofold relative to the initial level (Fig. 4). This indicates an intensive process of desamination of organic matter, leading to volatilization of ammonium nitrogen. Under such conditions, the forms N-NH_4^+ were subject to limited immobilization and incorporation into the structures of humus compounds [8], which is confirmed by the high losses of nitrogen between days 20 and 40 of composting (Fig. 7). The index of compost maturity, calculated on the basis of the content of N-NH_4^+ and N-NO_3^-, assumed a value below 0.16 in the third month of compost maturation.

In variant C, in which the content of water was maintained at 0.6 kg kg^{-1} dm, the processes of nitrogen transformation showed a different run, and the dynamics of temperature (Fig. 1) did not ensure sanitary safety of the compost. In that treatment, in the initial two months, the content of N_t and N-NH_4^+ in water extracts increased, and in further periods of compost maturation their content decrease. Losses of nitrogen increased at a high rate from day 82 of composting, and after five months attained the level of 31 % in relation to the content of nitrogen in the initial material.

Analyzing the dynamics of changes in the content of water-soluble forms of N-NH_4^+ and N-NO_3^- during composting of wastes (Fig. 4–5), we can assume a strong effect of denitrification process on the level of losses of N_t at higher moisture levels. The moisture level range of 0.46–0.6 kg H_2O kg^{-1} dm and changes in aeration conditions at intervals of 10–15 days when the composted material was stirred, could have determined the processes of nitrification and denitrification. This is evidenced in the low content of N-NO_3^- in the composts of the variant in question, compared with the content of N-NO_3^- in the composts on the pile.

The results of the above observations indicate that during composting of MSW the processes of ammonia volatilization, immobilization, nitrification and denitrification take place at various rates.

The results obtained indicate also that modification of the parameters of composting, such as moisture level, temperature and content of oxygen [2, 8, 16, 18] has an significant effect on the properties of the final products of composting.

Conclusions

1. The level of moisture content of composted municipal wastes plays an important role in the shaping of the utility properties of composts and determines the content of total N and the transformation of its organic and mineral forms.

2. Composting of municipal wastes on the pile, at moisture level of 0.5 kg H_2O kg^{-1} dm, accelerated the maturation of composts and was conducive to the obtainment of product richer in nitrogen, with a higher content of N-NO_3^-.

3. Higher moisture content of composted municipal wastes (0.6 kg H_2O kg^{-1} dm) did not ensure their sufficient oxygenation, which led to greater losses of nitrogen, reduced the quality of compost, and did not ensure sanitary safety.

4. Higher moisture content (0.6 kg H_2O kg^{-1} dm) limited and modified the rate of biochemical transformations in composted municipal wastes and caused intensification of transformation of nitrogen compounds.

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WPŁYW UWILGOTNIENIA ODPADÓW KOMUNALNYCH NA PRZEMIANY FORM AZOTU W CZASIE KOMPOSTOWANIA

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Uniwersytet Przyrodniczy we Wrocławiu

Abstrakt: Analizowano wpływ uwilgotnienia komunalnych odpadów miejskich na szybkość przemian różnych form azotu w czasie kompostowania.

Kompostowanie materiału grzejnego opuszczającego linię technologiczną kompostowni MUT-DANO prowadzono przez okres 5 miesięcy w następujących warunkach: A – na pryźmie przy uwilgotnieniu 0,5 kg $H_2O \cdot kg^{-1}$ s.m., B – w pojemnikach ażurowych przy uwilgotnieniu 0,5 kg $H_2O \cdot kg^{-1}$ s.m., C – w pojemnikach ażurowych przy uwilgotnieniu 0,6 kg $H_2O \cdot kg^{-1}$ s.m. w dniach napowietrzania. Materiał mieszano w odstępach 10–15-dniowych, uzupełniano ubytki wody i pobierano próbki do badań. Oznaczono w nich: wilgotność aktualną, zawartość popiołu oraz różnych form azotu: N-ogółem, N – w wyciągu wodnym (1:10), $N\text{-}NH_4^+$ i $N\text{-}NO_3^-$ w wyciągu wodnym. Na podstawie uzyskanych wyników obliczono straty azotu ogółem.

Uzyskane wyniki badań wskazują, że poziom uwilgotnienia kompostowanych odpadów komunalnych odgrywa ważną rolę w kształtowaniu wartości nawozowej kompostów i decyduje o zawartości N-ogółem oraz transformacji jego form organicznych i mineralnych. Kompostowanie odpadów komunalnych na pryźmie ograniczało straty azotu, sprzyjało powstawaniu kompostów bardziej zasobnych w azot, o wyższej zawartości $N\text{-}NO_3^-$, gwarantowało ich pełne bezpieczeństwo sanitarne oraz decydowało o szybszym ich dojrzewaniu. Większe uwilgotnienie ograniczało i modyfikowało tempo przemian biochemicznych w kompostowanych odpadach komunalnych i zmieniało kierunek transformacji związków azotu. Zauważono, iż wyższa wilgotność kompostowanych odpadów komunalnych przyczyniała się do gorszego ich natlenienia i prowadziła do większych strat azotu, co obniżało wartość nawozową kompostu i nie gwarantowało bezpieczeństwa sanitarnego.

Słowa kluczowe: kompostowanie odpadów komunalnych, transformacja azotu, poziom uwilgotnienia

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EFFECT OF DIVERSIFIED FERTILISATION WITH NITROGEN ON CHANGES IN PHOSPHORUS CONTENT AND PHOSPHATASE ACTIVITY IN CORN (*Zea mays* L)

WPŁYW INTENSYWNOŚCI NAWOŻENIA GLEBY ZRÓŻNICOWANYMI DAWKAMI AZOTU NA KSZTAŁTOWANIE ZAWARTOŚCI FOSFORU I AKTYWNOŚCI FOSFATAZY W KUKURYDZY CORN (*Zea mays* L)

Abstract: The aim of the present research was to determine the effect of mineral nitrogen fertilization on the content of total phosphorus and organic compounds and the acidic and alkaline phosphatase activity in corn. Besides, the research involved monitoring of seasonal changes in the analyzed parameters in the dry matter of corn. The soil on which the test plant was grown was fertilised with cattle FYM applied once every four years in potato growing: 20, 40 Mg $\cdot$ ha^{-1} – factor I, and varied mineral ammonium nitrate doses: (N0) – 0, (N1) – 45, (N2) – 90, (N3) – 135 kg N $\cdot$ ha^{-1} – factor II. There was found a significant effect of mineral nitrogen fertilisation in a form of ammonium nitrate on the content of phosphorus in corn. The highest significant content of total phosphorus and phosphorus of organic compounds was found in the biomass of corn from N2 nitrogen treatments. The highest dose of nitrogen applied in the experiment (N3) resulted in a significant decrease in the phosphorus fraction in corn researched. The activity of alkaline phosphatase in corn ranged from 10.9 to 35.5 mM pNP $\cdot$ kg^{-1} $\cdot$ h^{-1}, while the activity of acid phosphomonoesterase was higher and ranged from 29.5 to 130 mM pNP $\cdot$ kg^{-1} $\cdot$ h^{-1}, irrespective of the corn harvest date.

Keywords: nitrogen, phosphorus, phosphatases, fertilization, corn

The nitrogen fertilisation is one of the basic yield-forming factors which also affect the chemical composition of the biomass of crops. Over the recent years the importance of corn (*Zea mays* L) as a fodder crop in many parts of the country has been clearly growing. Corn (maize), as a crop grown in moderate climate, demonstrates the greatest reaction to phosphorus fertilisation, which can enhance grain formation in the ear, which, in turn, is connected with an increase in the content of protein, vitamins, and

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a decreased content of water in grain. Corn, it is a crop with high nutrition requirements [1]. Under the conditions of intensive plant production, there have emerged tendencies to increase the level of nitrogen fertilisation, without maintaining traditionally established proportions with the other nutrients. The estimation of nitrogen fertilization on the quality of corn were studied before [2] as well as the influence of the application of natural and mineral fertilizers on the yield of corn were investigated [3]. However, the effect of simultaneous mineral and organic fertilization on P content and the activity of phosphatases in soil were not studied. Those is a lack of data, particularly on impact of such a fertilization on enzymatic activity of soils.

The aim of this paper was to determine the effect of FYM and nitrogen differentiated fertilisation doses on the content of total phosphorus and organic compounds and the activity of acid and alkaline phosphatase in corn. Similarly, the experiment aimed at investigating seasonal changes in the analysed parameters in the dry matter of corn.

Material and methods

To perform the research, plant samples were derived from a many-year long-term field experiment set up in 1980 by the Department of Plant Nutrition and Fertilisation of the Institute of Soil Science and Plant Cultivation in Pulawy. The experiment was conducted at the Agricultural Experiment Station at Grabowo on Vistula, the Mazowia province. The soils of the Agricultural Experiment Station in Grabowo, according to the 'Systematyki Gleb Polski' (Polish Soil Systematics) [according to PTG 1989] [4] represent Haplic Luvisols. The experiment was set up in a four-year crop rotation: potato, winter wheat, spring barley, corn grown for silage. Corn (Nimba FAO 260) for silage was harvested twice during the plant development in the 24^{th} year of the experiment: in June at the 5-leaf phase and in September at the phase of yellow maturity. To provide corn with nutrients, the following organic-mineral fertilisation was applied: cattle FYM at the doses of 20, 40 $Mg \cdot ha^{-1}$ (factor I), nitrogen in a form of ammonium nitrate: N0 – 0, N1 – 45, N2 – 90, N3 – 135 $kg\ N \cdot ha^{-1}$ – factor II. Phosphorus and potassium fertilisers were applied at the same doses for all the experimental fertilisation treatments: 24 $kg \cdot P \cdot ha^{-1}$ and 133 $K \cdot kg \cdot ha^{-1}$. In dry matter plant material the following were colorimetrically determined: the content of total phosphorus, phosphorus of organic compounds by Mehta et al method [5], activity of alkaline and acid phosphatase according to the Tabatabai and Bremner method [6]. The results were verified statistically with the analysis of variance in the randomized split-plot design, using the Microsoft Excel-based FR-ANALWAR statistics software. The comparison of means was performed based on the Tukey test at $p = 0.05$.

In order to define the relationship between the parameters researched for the present results, the analysis of simple correlation was made with 'Statistica for Windows' software.

Results and discussion

The statistical analysis confirmed the significant effect of fertilisation with varied mineral nitrogen doses on the content of total phosphorus in the dry matter of corn; both the dry matter sampled in June and in September. The highest content of phosphorus was recorded in the plant researched, sampled in June from the nitrogen treatments at the dose of N2 (3.8 g P $\cdot$ kg^{-1} mean for FYM doses) (Table 1). The application of the highest dose (N3) resulted in a 14 % decrease in the content of this nutrient as compared with the content recorded for nitrogen fertilisation at the dose of N2. The content of P_{total} in corn harvested in September was similar. Another similar relationship for the nitrogen dose of 120 kg $\cdot$ ha^{-1} was reported by Knapowski et al [7] who claim that a lack of equilibrium regarding mineral fertilisation, especially by applying high nitrogen doses, can decrease the content of phosphorus in plants and disturb the equilibrium between minerals. Excessively high doses of ammonium nitrate acidify the soil environment, which, as a result, inhibits the availability of phosphorus in plants, since the element is especially sensitive to changes in the soil reaction. Sometimes increased nitrogen fertilisation results only in a high increase in yielding, while the content of P_{total}, as a result of 'the dilution effect' can be even lower than when no nitrogen fertilisation is applied [8]. The concentration of the total content of phosphorus in corn sampled in September (yellow maturity phase) was 54 % lower as compared with the content of P_{total} in the biomass of that cereal plant researched collected in June (5-leaf phase). As reported by Podlesna and Winiarski [9], there was also observed a decreased content of P_{total} in the course of the vegetative development of corn. In the plants of this experiment, the authors observed that the difference in the concentration of total phosphorus in corn, between 6–8 leaf phase and flowering, accounted for an average of 75 %.

Table 1

Content of the total phosphorus [g P_{total} $\cdot$ kg^{-1} dm] in corn

FYM Factor I	Nitrogen Factor II									
	June					September				
	N0	N1	N2	N3	Mean	N0	N1	N2	N3	Mean
20	2.98	3.34	3.69	3.12	**3.28**	1.24	1.33	1.47	1.37	**1.35**
40	3.15	3.51	3.92	3.29	**3.49**	1.33	1.44	1.83	1.66	**1.56**
Mean	**3.06**	**3.43**	**3.80**	**3.25**	**3.39**	**1.29**	**1.38**	**1.65**	**1.51**	**1.46**
$LSD_{0.05}$ Factor I	0.080					ns*				
Factor II	0.173					0.066				

* ns – non-signification.

The content of phosphorus of organic compounds in corn was also significantly affected by the application of varied nitrogen fertilisation. Increasing the nitrogen dose from 0 to 90 kg N $\cdot$ ha^{-1} (N2) significantly increased the content of P_{org} (Table 2) in corn sampled in September.

However, increasing the nitrogen dose to 135 kg N $\cdot$ ha^{-1} (N3) decreased the content of phosphorus present in organic bonds by 11 % as compared with the highest concentration of this fraction of phosphorus (1.25 g P $\cdot$ kg^{-1} mean for FYM doses, at the nitrogen dose of 90 kg N $\cdot$ ha^{-1}).

Table 2

Content of organic phosphorus [g P_{org} · kg^{-1} dm] in corn

FYM Factor I	Nitrogen Factor II									
	June					September				
	N0	N1	N2	N3	Mean	N0	N1	N2	N3	Mean
20	0.168	0.183	0.210	0.195	**0.189**	0.867	1.06	1.20	0.97	**1.03**
40	0.171	0.194	0.226	0.205	**0.199**	0.857	0.99	1.31	1.26	**1.10**
Mean	**0.170**	**0.188**	**0.218**	**0.200**	**0.194**	**0.862**	**1.02**	**1.25**	**1.12**	**1.06**
$LSD_{0.05}$ Factor I	ns					0.043				
Factor II	0.011					0.059				

* ns – non-signification.

The activity of alkaline phosphatase in corn ranged from 10.9 to 35.5 mM pNP · kg^{-1} · h^{-1} (Table 3), while the activity of acid phosphomonoesterase was higher and ranged from 29.5 to 130 mM pNP · kg^{-1} · h^{-1}, irrespective of the corn harvest date (Table 4), however the activity of both enzymes responsible for phosphorus transformations was higher in corn sampled in September. Smolik and Nowak [10] also report on the highest phosphatase activity at the last development phase of the plants researched. Clear changes in the phosphatase activity over plant tissue aging can be due to a change in the degree of aggregation of the molecule or the synthesis of enzyme *de novo*. Olczak [11] refers this phenomenon to the share of phosphatases in the cell autolysis, preceded by changes in the membrane permeability and the release of the lysosomal enzyme to the cytoplasm.

Table 3

Activity of alkaline phosphatase [mM pNP · kg^{-1} dm · h^{-1}] in corn

FYM Factor I	Nitrogen Factor II									
	June					September				
	N0	N1	N2	N3	Mean	N0	N1	N2	N3	Mean
20	10.9	14.7	14.1	12.6	**13.1**	25.9	29.4	27.6	26.7	**27.3**
40	11.7	15.7	15.3	14.4	**14.3**	28.3	35.5	33.1	31.5	**32.1**
Mean	**11.3**	**15.2**	**14.7**	**13.5**	**13.7**	**27.1**	**32.5**	**30.4**	**29.1**	**29.7**
$LSD_{0.05}$ Factor I	0.202					0.318				
Factor II	0.877					0.158				

The statistical analysis performed demonstrated a significant effect of FYM fertilisation on the activity of alkaline phosphatase in plants. The higher the FYM dose, the higher the activity of the enzyme researched (14.3 mM pNP · kg^{-1} · h^{-1} in the plant sampled in June, 32.1 mM pNP · kg^{-1} · h^{-1} in the plant sampled in September).

Fertilisation with mineral nitrogen in a form of ammonium nitrate which is a physiologically acid fertiliser resulted in significant changes in the activity of the plant phosphomonoesterases researched. Nitrogen applied at the highest dose N3 resulted in a significant decrease in the activity of alkaline phosphatase (Table 3), however, it increased the activity of acid phosphatase (Table 4).

Table 4

Activity of acid phosphatase [mM pNP · kg^{-1} dm · h^{-1}] in corn

FYM Factor I		Nitrogen Factor II									
		June					September				
		N0	N1	N2	N3	Mean	N0	N1	N2	N3	Mean
20		29.5	38.8	47.6	54.9	**42.7**	48.6	87.4	118	124	**94.6**
40		41.2	47.4	57.6	68.6	**53.7**	57.0	101	114	130	**100**
Mean		**35.4**	**43.1**	**52.6**	**61.7**	**48.2**	**52.8**	**94.0**	**116**	**127**	**97.6**
$LSD_{0.05}$	Factor I	ns*					ns				
	Factor II	3.710					6.375				

* ns – non-significant.

There were recorded high significant coefficients of correlation between the content of phosphorus of organic compounds and the activity of alkaline and acid phosphatase in corn (Table 5), which is confirmed by earlier reports by Hammond et al [12] who observed that intercellular phosphatases in plants participated in the mineralization of organic phosphorus bonds successfully. The analysis of correlation which involved the present results showed a significant negative relationship between the content of total phosphorus and the activity of the phosphomonoesterases researched in the corn biomass. Similar results were reported by Machado and Furlani [13] where the value of the coefficient of correlation between the activity of AcP and the content of P_{total} in corn was r = –0.73*.

Table 5

Coefficients of correlation between the parameters investigated

	P_{total}	P_{org}	AlP	AcP
AcP	–0.65*	0.85*	0.80*	1
AlP	–0.88*	0.96*	1	
P_{org}	–0.90	1		
P_{total}	1			

Conclusions

1. The content of total phosphorus and phosphorus of organic bonds depended significantly on nitrogen fertilisation. The highest concentration of both P_{total} and P_{org} was recorded when the nitrogen dose of 90 kg N · ha^{-1} was applied. The higher dose of 135 kg N · ha^{-1} decreased the content of the parameters researched.

2. The application of FYM in the experiment significantly changed the content of both total phosphorus and the phosphorus of organic compounds. Increasing doses of

natural fertiliser resulted in an increase in the concentration of that nutrient in the test plant irrespective of the sampling date.

3. The activity of both phosphomonoesterases was significantly modified by the experiment factors. Nitrogen applied at the dose of 135 kg N $\cdot$ ha^{-1} stimulated the activity of acid phosphatase, however, it inhibited the alkaline phosphatase in corn plants significantly.

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WPŁYW INTENSYWNOŚCI NAWOŻENIA GLEBY ZRÓŻNICOWANYMI DAWKAMI AZOTU NA KSZTAŁTOWANIE ZAWARTOŚCI FOSFORU I AKTYWNOŚCI FOSFATAZY W KUKURYDZY CORN (*Zea mays* L)

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Abstrakt: Celem przeprowadzonych badań było określenie wpływu nawożenia azotem na zawartość fosforu ogółem i związków organicznych oraz aktywność fosfatazy kwaśnej i alkalicznej w kukurydzy. Ponadto w badaniach uwzględniono monitoring sezonowych zmian analizowanych parametrów w suchej masie kukurydzy. Gleba, na której uprawiano roślinę testową, nawożona była obornikiem bydlęcym stosowanym raz na cztery lata w uprawie ziemniaka: 20 i 40 Mg $\cdot$ ha^{-1} – I czynnik, oraz zróżnicowanymi dawkami saletry amonowej: (N0) – 0, (N1) – 45, (N2) – 90, (N3) – 135 kg N $\cdot$ ha^{-1} – II czynnik. Stwierdzono duży wpływ nawożenia azotem w postaci saletry amonowej na zawartość fosforu w kukurydzy. Największą znaczną zawartość fosforu ogółem i fosforu związków organicznych stwierdzono w biomasie kukurydzy pobranej z obiektów nawożonych azotem mineralnym w dawce N2. Zastosowany w doświadczeniu azot w dawce (N3), spowodował istotne obniżenie badanych frakcji fosforu w kukurydzy. Aktywność fosfatazy alkalicznej w kukurydzy kształtowała się w zakresie 10,9–35,5 mM pNP $\cdot$ kg^{-1} $\cdot$ h^{-1}, natomiast aktywność kwaśnej fosfomonoesterazy była wyższa i mieściła się w zakresie od 29,5–130 mM pNP $\cdot$ kg^{-1} $\cdot$ h^{-1} niezależnie od terminu zbioru kukurydzy.

Słowa kluczowe: azot, fosfor, fosfatazy, nawożenie, kukurydza

E C O L O G I C A L C H E M I S T R Y A N D E N G I N E E R I N G A

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MINERALIZATION OF ORGANIC NITROGEN COMPOUNDS IN GYTTJA GYTTJA-MUCK SOILS IN RELATION TO THE CONTENT OF MINERAL NITROGEN IN GROUNDWATERS

MINERALIZACJA ORGANICZNYCH ZWIĄZKÓW AZOTU W GLEBACH GYTIOWO-MURSZOWYCH A ZAWARTOŚĆ AZOTU MINERALNEGO W WODACH GRUNTOWYCH

Abstract: The aim of the investigation was to present the rate of mineralization of organic nitrogen compounds in gyttja and half-bog soils situated under various habitat conditions of Mragowo and Olsztyn lakeland in the period of vegetation and during winter. The concentrations of $N\text{-}NO_3$ and $N\text{-}NH_4$ in the groundwaters of these soils were studied and compared with the dynamics of the mineralization process of organic matter in the soil. The findings have proved that the rate of the mineralization of organic nitrogen compounds in the soils under study varied in particular seasons of the year depending on the state of their moisture and the way of utilization. The most mineral N was released in the gyttja and half-bog soil under pasture in summer periods. The $N\text{-}NO_3$ form dominated in the process of the mineralization of organic nitrogen compounds. The pasture-purpose utilization of gyttja soil favoured the nitrification process and increased nitrate outwashing to groundwaters. It has been found out that in the groundwaters of the Mgyhh160ps soils under the pasture the average annual concentration of $N\text{-}NO_3$ amounted to 0.774 $mg \cdot dm^{-3}$ $N\text{-}NO_3$. The highest content of $N\text{-}NO_3$ in the groundwaters was found out mostly in the summer periods when the nitrification process in the soil occurred most intensely. A calculated coefficient of correlation between the content of $N\text{-}NO_3$ and $N\text{-}NH_4$ in water and in gyttja soils under pasture shows a positive correlation for $N\text{-}NO_3$. In the case of gyttja soils under birch alder carr there was a similar interdependence as in the soil under the pasture except that only the power of the relation between the content of $N\text{-}NH_4$ in the soil to the concentration in the water was statistically significant. In the case of unused gyttja soils and those under the meadow, the correlation between the content of nitrogen $N\text{-}NO_3$ in the soil and water was negative. A calculated correlation coefficient for gyttja soils irrespective of the way of their use proved that the increase in the concentration of $N\text{-}NO_3$ in the soil involved a growth of the concentration of $N\text{-}NO_3$ in the water. In the case of $N\text{-}NH_4$, in spite of the increase of this form of nitrogen in the soil, a decrease in its concentration in the water was observed.

Keywords: mineralization, gyttja-muck soils, habitat conditions, groundwater

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Mineralization of organic nitrogen compounds in soil leads to a release of mineral nitrogen, which is the main nutrient of plants. The dynamics of this process in organic soils is dependent on prevailing habitat conditions, the way of their utilization, and can vary in particular years and seasons of the year [1, 2]. In the soils abundant in organic matter, mineralization of organic nitrogen compounds occurs with a higher efficiency of the process of nitrification than ammonification [3]. Under the conditions which favour mineralization of organic matter, there may be an excessive and uncontrolled release of mineral nitrogen above the requirement of the plants. Under such conditions, the excess of this component, partcularly in the nitrate form, can be washed out from the soil to the groundwaters, thus contributing to their eutrophication. Gyttja areas, which are a peculiarity of young glacial terrains, were first dried at the end of the 19th century in order to gain new agricultural land for meadows and pastures. Due to difficulties connected with cultivating these soils, under current new economic conditions extensive meadow utilization is carried out on part of gyttja soils, while some other gyttia soils are excluded from farming and left as wasteland without a proper regulation of water relations. Therefore, it is necessary to do research on the course and rate of the process of the mineralization of organic nitrogen compounds in gyttja soils characterized by changed water conditions in order to control it and predict the effects of those changes for the environment. In the scientific literature, research of this kind in gyttja soils has been described sporadically so far.

The aim of this paper has been to present the dynamics of the mineralization of organic nitrogen compounds in the vegetation period and in winter in gyttja soils depending on their management against the background of existing habitat conditions and to determine the content of nitrate and ammonia nitrogen in groundwaters.

Material and methods

The dynamics of the contents of mineral nitrogen compounds was studied in the years 2002–2008 in gyttja and half-bog soils and groundwaters in the Gazwa object located in the Mragowo Lakeland mesoregion and 2006–2008 in the Lajsy and Peglity objects in the Olsztyn Lakeland mesoregion [4]. The Gazwa gyttja of an area of 104 ha was formed in 1860 as a result of emptying ribbon lake Stama [5]. After 1910, gyttja soils were drained and put into grassland. Lack of proper maintenance of melioration facilities caused an increase in the groundwater level and a repeated turning of these soils into a marsh. At present, extensive meadow-pasture utilization is carried out only in peripheric parts of the gyttja area, while part of the object is afforested. Research on the Gazwa object was carried out in the gyttja medium mouldy soil (MgyIIhh160ps) located under an extensively used pasture and in the gyttja and half-bog soil (MgyIIhh190pl) under a birch alder carr. In the Lajsy and Peglity objects, research was carried out on the gyttja area of 10 ha, located in the valley of the River Gilawka. Drained gyttja soils, in the post-war period belonging to the Lajsy State Farm and individual farmers from the village of Peglity, were intensively used as grassland. At present, due to difficulties with maintaining a constant low level of the groundwater in the whole gyttja area, part of it has been flooded and fish ponds have been established.

In the village of Lajsy, research was carried out in gyttja and half-bog low mouldy soil (MgyIhh), excluded from farm production, located on the margins of ponds, and in the Peglity object – in gyttja and half-bog medium mouldy soil (MgyIIhh), located under an extensively used meadow. The dynamics of the mineralization of organic nitrogen compounds in gyttja soils and the content of $N-NO_3$ and $N-NH_4$ in the groundwaters of these soils were studied in the four seasons of the year. In soil pits made in places representative for the whole objects, soil samples were collected with maintaining the structure, in four repetitions, from layers: 5–10, 15–20, 25–30, 35–40, 50–60 cm in soils MgyIIhh160ps and MgyIIhh190ps, and from layers 5–10, 15–25, 30–40 cm in soils MgyIhh and MgyIIhh, using cylinders of the volume of 100 cm^3. The following was determined in the samples: soil ash content by burning soil samples at the temperature of 550 ^oC, volumetric density after drying the samples at 105 ^oC, general porosity was calculated on the basis of volumetric density and soil ash content, soil-moisture was determined in four seasons of the year using the drier method [6]. The soil reaction was determined by means of the potentiometric method in H_2O and KCl with a concentration of 1 mol · dm^{-3}, and total nitrogen – with the Kjeldahl method. The content of mineral nitrogen compounds ($N-NO_3$ and $N-NH_4$) in the soil in the seasons of the year was examined in the extract of 1 % K_2SO_4 after a 14-day incubation at the temperature of 28 ^oC [7]. The $N-NO_3$ content was estimated by adopting limiting numbers according to Gotkiewicz [1]. The levels of groundwater were systematically measured and water was sampled for chemical analyses in piezometers installed in the vicinity of the the soil pits. Nitrate nitrogen in the groundwaters was determined calorimetrically with phenyldisulphonic acid, ammonia nitrogen – calorimetrically with Nessler's reagent [8]. The findings of the research concerning the course of the mineral nitrogen release process ($N-NO_3$, $N-NH_4$), presented in this paper, were a continuation of extended investigations on the intensity of the mineralization of organic nitrogen compounds in gyttja soils in different seasons of the year against the background of varied habitat conditions of young glacial terrains [9].

Results and discussion

Gyttja and half-bog medium mouldy soil made from detritus gyttja, underlain with slightly argillaceous sand (MgyIIhh160ps) at the depth of 160 cm occurs in the Gazwa object under the pasture. In the gyttja and half-bog soil under the birch alder carr down to 25 cm there is gyttja half-bog, highly hydrated detritus gyttja occurs below it. At the depth of 190 cm there is slightly argillaceous sand with gleying characteristics (MgyIIhh190 ps). Gyttja and half-bog slightly mouldy soil made from detritus and limestone gyttja occurring in the whole soil profile (MgyIhh) is in the village of Lajsy in the valley of the River Gilawka. In the village of Peglity under grassland there is gyttja and half-bog medium mouldy soil, also made from detritus and limestone gyttja (MgyIIhh). In the Gazwa object, gyttja and half-bog soils in the surface layers were characterized by a high soil ash content (62.4–65.5 % dm), which was caused by an accumulation of mineral parts from neighbouring areas (Table 1). In the deeper layers of the soils studied, the soil ash content decreased to 11.7 % in the MgyIIhh160 ps soil and 20.8 % dm in the MgyIIhh190 ps soil. The volumetric density in the silted up layers of gyttja soils in the Gazwa object was high (0.44–0.49 g · dm^{-3}) and lessened in the deeper layers to 0.09 g · dm^{-3}. General porosity in the layers of 5–10 cm of the soils under study in the Gazwa object was 70 % on average and went up to 94 % of the volume in the layers of 50–60 cm. The reaction of gyttia soils in the Gazwa object was acid in the layers to 20 cm and slightly acid in deeper layers (Table 1).

Table 1

Physical and chemical properties of gyttja-muck soil on the Gazwa, Lajsy, Peglity objects

Layer [cm]	Level	Ash content [% dm]	Volume density [g · cm^{-3}]	Specific density [g · cm^{-3}]	Total porosity [%]	pH in 1 M KCl	pH in H_2O	N-Total [%]
Soil gyttja-muck (MgyIIhh160ps) under pasture – Gazwa object								
5–10	Mgy	62.4	0.44	1.52	71.0	4.7	5.2	1.65
15–20	Mgy	11.7	0.18	1.46	88.0	4.9	5.2	3.53
25–30	Mgy	12.9	0.13	1.46	91.0	5.8	6.5	3.99
35–40	Gy	11.5	0.11	1.46	93.0	5.9	6.5	3.59
50–60	Gy	11.7	0.09	1.46	94.0	6.4	6.7	3.59
Soil gyttja-muck (MgyIIhh160ps) under alder swamp– Gazwa object								
5–10	Mgy	65.5	0.49	1.52	70.0	5.1	6.2	0.94
15–20	Mgy	49.3	0.49	1.50	67.0	5.9	6.3	0.91
25–30	Gy	26.3	0.22	1.48	85.0	6.1	6.5	3.36
35–40	Gy	20.8	0.09	1.47	94.0	6.1	6.5	3.84
50–60	Gy	20.8	0.09	1.47	94.0	6.4	6.7	3.83
Soil gyttja-muck (MgyIhh) barren – Lajsy object								
5–10	Mgy	36.44	0.19	1.49	87.0	7.77	7.94	0.30
15–25	Gy	20.50	0.15	1.47	90.0	7.97	8.16	0.23
30–40	Gy	27.87	0.18	1.48	88.0	8.05	8.18	0.28
Soil gyttja-muck (MgyIIhh) under meadow – Peglity object								
5–10	Mgy	35.54	0.18	1.49	88.0	7.18	7.90	0.44
15–25	Mgy	30.08	0.15	1.48	90.0	7.21	8.03	0.34
30–40	Gy	28.29	0.16	1.48	89.0	7.30	8.14	0.24

Explanations: Gy – gyttja. Mgy – gyttja-muck.

In the analyzed gyttja soils in the Lajsy and Peglity, the content of mineral components was higher in the mouldy layers and amounted to 36.4 % in the MgyIhh soil and 35.5 % in the MgyIIhh soil. In the deeper organic layers, the soil ash content was smaller and smaller and amounted to 27.9 % in the MgyIhh soil and 28.3 % d.m. in the MgyIIhh soil. The volumetric density of the gyttja soils in the Lajsy and Peglity objects was higher in the mouldy layers (0.19 g · dm^{-3} in the MgyIhh soil, 0.17 g · dm^{-3} in the MgyIIhh soil). General porosity in the gyttja and half-bog soils in the Lajsy and Peglity objects was lower in the mouldy layers and higher in the organic deposits placed deeper. Gyttja and half-bog soils in the Lajsy and Peglity objects were characterized by alkaline reaction (Table 1). The content of total N in the gyttja soil under the pasture in the Gazwa object in the layer of 5–10 cm amounted to 1.65 % and grew to 3.99 % in the layers of 25–30 cm. In the gyttja soil under forest in this object, the content of total N ranged from 0.9 % in the layer of 5–20 cm, to 3.84 % in the layer of 35–40 cm. These are high contents of total N, which occur in detritus gyttjas [5]. In the gyttja soils in the Lajsy and Peglity objects, the content of total N was lower and in mouldy layers amounted to 0.30 % in the MgyIhh soil, 0.44 % in the Mgyhh soil, and in organic layers of 30–40 cm – 0.28 % in the MgyIhh soil, 0.24 % in the Mgyhh soil. During the investigation period the soils differed in moisture, which was connected with the depth of the groundwater deposit (Table 2).

Table 2

Average moisture and grundwater levels [cm] on the Gazwa, Lajsy, Peglity objects

Management	Layer [cm]	Seasons of the year			
		Spring	Summer	Autumn	Winter
		Moisture soil [%]			
Soil gyttja-muck (MgyIIhh160ps)					
Soil under pasture	5–10	54.12	42.87	44.59	50.22
	15–20	69.36	59.61	55.99	53.12
	25–30	86.53	78.78	71.20	71.60
	35–40	91.67	85.51	81.27	87.77
Soil gyttja-muck (MgyIIhh160ps)					
Soil under forest	5–10	83.48	74.05	77.85	78.63
	15–20	85.10	78.38	74.61	78.70
	25–30	88.23	83.62	80.53	85,00
	35–40	90.40	92.40	89.32	89,75
Soil gyttja-muck (MgyIhh)					
Barren	5–10	89.87	88.21	91.37	95.34
	15–20	91.34	90.78	93.87	96.87
	25–40	95.41	91.89	95.88	97.33
Soil gyttja-muck (MgyIIhh)					
Soil under meadow	5–10	68.89	48.97	49.85	89.31
	15–20	86.91	51.78	55.97	92.84
	35–40	95.81	81.93	86.54	97.14
Groundwater level (cm)					
Piezometer I		35	50	48	48
Piezometer II		10	15	12	**
Piezometer III		8	11	7	**
Piezometer IV		25	40	35	8

** – Water on the surface of soil.

A low level of groundwaters was maintained in the gyttja soils under the grassland. During the vegetation time, the groundwater in those soils remained below 25 cm on average. In the summer periods there occurred the maximum decrease in the level of groundwaters and it stayed below 40 cm from the surface. In winter the level of the groundwater in the soil under the pasture in the Gazwa object stayed at the depth of 48 cm on average, while in the gyttja soil under the meadow in the Peglity object – 8 cm. The gyttja soils under the grassland were characterized by low moisture of the layers of 5–10 cm in spring, while in summer there was an overdrying of these layers. In winter, a significant increase in moisture, which was from 89.3 to 97.14 %, occurred only in the gyttja soil under the meadow in the Peglity object. The level of groundwater in the MgyIhh and MgyIIhh190ps was higher and did not show a considerable variation in particular seasons of the year. The moisture of the surface layers of these soils ranged from 74.05 to 91.4 % of the volume and increased at the deeper layers to 95.9 % of the volume (Table 2). The rate of the mineralization of organic nitrogen compounds in the studied gyttia soils varied depending on the way of their utilization. The most mineral N was released in the gyttia and half-bog soil under the pasture at Gazwa and in the gyttja and half-bog soil under the meadow at Peglity (Table 3). During the vegetation period, the content of mineral N in these soils ranged from 8.78 to 96.77 mg · dm^{-3}. The investigations indicate that the rate of mineralization of organic nitrogen compounds varied in particular seasons. The most mineral N was released in summer in the MgyIIhh soil under the pasture (77.58 mg · dm^{-3} – the layer of 5–10 cm, 96.77 mg · dm^{-3} – the layer of 15–20 cm) and in the MgyIIhh soil under the meadow (32.59 mg · dm^{-3} on average – the layer of 5–20 cm). In spring, an average of 28.02 mg · dm^{-3} of mineral N was released from the layers of 5–10 cm in the MgyII160ps soil, and in the MgyIIhh soil – 21.74 mg · dm^{-3}, while in autumn – 20.95 mg · dm^{-3} and 16.86 mg · dm^{-3}, respectively. It was the amount of released $N\text{-}NO_3$ that was particularly large in the process of the mineralization of organic nitrogen content. The highest content of $N\text{-}NO_3$ was in the gyttja and half-bog soil under the pasture in summer in the layers to 5–20 cm and it ranged from 48.20 to 72.03 mg · dm^{-3}, which means that according to adopted standards [2] it was a very high abundance. In the deeper layers, the content of $N\text{-}NO_3$ stayed within high abundance. In the remaining seasons of the year the content of $N\text{-}NO_3$ in the gyttja and half-bog soil under the pasture stayed within medium abundance. In the gyttja and half-bog soil under the meadow, the content of $N\text{-}NO_3$ ranged from 19.68 mg · dm^{-3} to 10.18 mg · dm^{-3} in summer, which means a medium abundance. In spring, the content of $N\text{-}NO_3$ in the gyttja soil under the meadow stayed within medium abundance only in the layers of 5–30 cm and ranged from 11.87 to 13.12 mg · dm^{-3}. In the deeper layers, the content of $N\text{-}NO_3$ was very low (3.45 mg · dm^{-3}). In autumn, the content of $N\text{-}NO_3$ in the gyttja and half-bog soil under the meadow was in the layers of 5–10 cm medium (12.9 mg · dm^{-3}), in the layers of 15–30 cm – low (7.63 mg · dm^{-3}) and in the layers of 35–40 cm – very low (3.39 mg · dm^{-3}). An intense release of mineral nitrogen also occurred in winter in the gyttja and half-bog soil under the pasture. The content of mineral N in the soil in that period ranged from 18.90 to 23.03 mg · dm^{-3}. The release of $N\text{-}NH_4$ was higher and ranged from 12.49 to 14.98 mg · dm^{-3}. The content of nitrates was low and medium. In order to estimate the

Table 3

Mineral nitrogen content of gyttja-muck soil on the Gazwa, Lajsy, Peglity objects

Season	Layer [cm]	Soil gyttja-muck (MgyIIhh160ps) under pasture				Soil gyttja-muck (MgyIIhh190ps) under alder swamp				Soil gyttja-muck(MgyIIhh) barren				Soil gyttja-muck (MgyIIhh) under meadow			
		$N\text{-}NO_3$	$N\text{-}NH_4$	N-min.	$N\text{-}NO_3/N\text{-}NH_4$	$N\text{-}NO_3$	$N\text{-}NH_4$	N-min.	$N\text{-}NO_3/N\text{-}NH_4$	$N\text{-}NO_3$	$N\text{-}NH_4$	N-min.	$N\text{-}NO_3/N\text{-}NH_4$	$N\text{-}NO_3$	$N\text{-}NH_4$	N-min.	$N\text{-}NO_3/N\text{-}NH_4$
Spring	5–10	16.10	11.92	28.02	1.35	6.78	13.49	20.27	0.50	1.36	1.69	3.05	0.80	11.87	9.87	21.74	1.20
	15–20	15.17	11.44	26.61	1.33	6.95	10.22	17.17	0.68	1.15	1.42	2.57	0.81	10.44	9.94	20.38	1.05
	25–30	17.78	9.42	27.20	1.89	3.82	9.10	12.92	0.42	0.09	1.26	1.35	0.07	13.112	8.87	21.99	1.48
	35–40	16.51	9.79	26.30	1.68	3.77	8.23	.12.00	0.46	0.15	1.24	1.39	0.12	3.45	8.94	12.39	0.39
Summer	5–10	48.20	29.38	77.58	1.64	14.48	14.36	28.84	1.01	1.56	1.59	3.15	0.98	19.68	12.87	32.55	1.53
	15–20	72.03	24.74	96.77	2.91	21.05	12.31	33.36	1.71	1.21	1.80	3.01	0.67	19.11	13.52	32.63	1.41
	25–30	24.43	8.64	33.07	2.83	9.95	16.34	26.29	0.61	0.04	1.70	1.74	0.02	19.22	7.85	27.07	2.45
	35–40	25.18	4.10	29.28	6.14	3.17	10.74	13.91	0.30	0.06	1.02	1.08	0.06	10.18	3.48	13.66	2.93
Autumn	5–10	14.51	6.44	20.95	2.25	12.31	15.30	27.61	0.88	1.01	1.37	2.38	0.74	12.90	3.96	16.86	3.26
	15–20	11.44	11.07	22.51	1.03	17.24	22.28	39.52	0.77	0.81	1.62	2.43	0.50	9.90	7.71	17.61	1.28
	25–30	13.25	11.02	24.27	1.20	6.39	13.89	20.28	0.46	0.55	0.84	1.39	0.65	5.37	10.14	15.51	0.53
	35–40	13.64	4.05	17.69	3.37	4.03	12.96	16.99	0.31	0.29	0.94	1.25	0.30	3.39	5.39	8.78	0.63
Winter	5–10	8.49	14.54	23.03	0.58	—	—	—	—	0.65	1.15	1.80	0.56	0.30	6.05	6.35	0.05
	15–20	10.58	14.98	25.56	0.71	0.10	2.39	2.496	0.04	0.33	0.78	1.11	0.42	0.14	5.24	5.38	0.03
	25–30	10.35	12.49	22.84	0.83	0.12	2.31	2.43	0.05	0.26	1.06	1.32	0.24	0.02	3.36	3.38	0.01
	35–40	6.25	12.65	18.90	0.49	0.05	2.55	2.60	0.02	0.16	0.71	0.87	0.22	0.13	5.59	5.72	0.02

Table 4

Average nitrogen content of groundwater on the Gazwa, Lajsy, Peglity objects

Season	Soil gyttja-muck (MgyIIhh160ps) under pasture			Soil gyttja-muck (MgyIIhh190ps) under alder swamp			Soil gyttja-muck(MgyIhh) barren			Soil gyttja-muck (MgyIIhh) under meadow		
	$N\text{-}NO_3$	$N\text{-}NH_4$	N-min.	$N\text{-}NO_3$	$N\text{-}NH_4$	N-min.	$N\text{-}NO_3$	$N\text{-}NH_4$	N-min.	$N\text{-}NO_3$	$N\text{-}NH_4$	N-min.
	$[mg \cdot dm^{-3}]$			$[mg \cdot dm^{-3}]$			$[mg \cdot dm^{-3}]$			$[mg \cdot dm^{-3}]$		
Spring	1.461	0.216	1.677	0.344	0.340	0.684	0.132	0.367	0.499	0.010	0.288	0.298
Summer	1.503	1.260	2.763	0.523	0.842	1.365	0.122	0.550	0.672	0.010	0.390	0.400
Autumn	1.032	1.372	2.404	1.233	1.294	2.527	0.120	0.567	0.687	0.005	0.220	0.225
Winter	1.102	1.245	2.347	0.532	0.345	0.877	0.420	0.220	0.640	0.020	0.200	0.220
Average	0.774	0.773	1.548	0.658	0.705	1.363	0.199	0.426	0.624	0.011	0.275	0.286

conditions of the process of the mineralization of organic nitrogen compounds, the ratio of $N\text{-}NO_3$ to $N\text{-}NH_4$ is calculated [7]. During the vegetation period, it was above unity in the gyttja and half-bog soils under the pasture, while in the gyttja and half-bog soil under the meadow it ranged below unity only in the deeper layers. This proves a high biological activity of the soils and favourable conditions for nitrification. The least mineral N (1.39–3.15 mg $\cdot$ dm^{-3}) was released in the gyttja and half-bog unused soil. The content of $N\text{-}NO_3$ in all studied layers stayed within very low abundance. $N\text{-}NH_4$ the amount of which in the four seasons of the year ranged from 0.71 to 1.69 mg $\cdot$ dm^{-3}, dominated in the process of the mineralization of organic nitrogen compounds in this soil. The ratio of released $N\text{-}NO_3$ to $N\text{-}NH_4$ was below 1, which proves a limited course of the nitrification process. Under the conditions of an intense process of the mineralization of organic nitrogen compounds in the half-bog soils, excess mineral nitrogen in the form of ions NH_4^+ and NO_3^- not used by plants can permeate to groundwaters, thus causing their eutrophication [10]. During the investigation it was found out that the pasture-purpose utilization of gyttja soils favoured the process of nitrification and increased nitrate washout to groundwaters. It was ascertained that in the groundwaters in the Mgyhh160ps soils under the pasture, the average annual concentration of $N\text{-}NO_3$ amounted to 0.774 mg $\cdot$ dm^{-3}, in the MgyIIhh190ps soil under the birch alder carr – 0.658 mg $\cdot$ dm^{-3}, in the unused MgyIhh soil – 0.199 mg $\cdot$ dm^{-3}, and in the MgyIIhh soil under the meadow – 0.011 mg $\cdot$ dm^{-3}. The highest contents of $N\text{-}NO_3$ in groundwaters was found out mostly in summer seasons when the nitrification process in the soil was most intense. Considering the interdependence of the content of $N\text{-}NO_3$ and $N\text{-}NH_4$ in the soil and in the water in the context of the way of the utilization of the soil, the correlation coefficient for the gyttja soils under the pasture shows a positive correlation for $N\text{-}NO_3$ ($r = 0.73$) and $N\text{-}NH_4$ ($r = 0.55$). In the case of the gyttja soils under the birch alder carr there was a similar interdependence as in the soil under the pasture except that the power of the relation between the content of $N\text{-}NH_4$ in the soil to the concentration in water was statistically significant and amounted to $r = 0.56$.

In the case of gyttja soils unused and under the meadow, the correlation between the content of nitrogen $N\text{-}NO_3$ in the soil and water was negative. The $N\text{-}NO_3$ form in the soil on these analysed utilizations was characterized by coefficients of correlation equal to $r = -0.90$ and $r = -0.62$, respectively. The $N\text{-}NH_4$ form in the unused gyttja soils showed a statistically significant negative correlation ($r = -0.85$). The overall analysis of the gyttja soils irrespective of the way of their utilization proved that the growth of the concentration of $N\text{-}NO_3$ in soil involves the growth of the concentration of $N\text{-}NO_3$ in water ($r = 0.62$; $p = 0.011$). In the case of $N\text{-}NH_4$ a decrease in the concentration in water was observed in spite of an increase of this nitrogen form in soil. However, the coefficient of correlation $r = -0.45$ was statistically insignificant.

Conclusions

1. The most mineral N was released in the gyttja and half-bog soil under the pasture in the summer seasons. The $N\text{-}NO_3$ form dominated in the process of the mineralization

of organic nitrogen compounds. In the mouldy layers, the content of NO_3 stayed within very high abundance, and in the gyttja layers – within high abundance. In the other seasons of the year the content of N-NO_3 in the gyttja and half-bog soil under the pasture stayed within medium abundance. In the gyttja and half-bog soil under the meadow the content of N-NO_3 stayed within medium abundance in summer.

2. An intense release of mineral nitrogen occurred also in winter in the gyttja and half-bog soil under the pasture. The content of mineral N in the soil in that period ranged from 18.90 to 23.03 mg $\cdot$ dm^{-3}. The release of N-NH_4 was higher and ranged from 12.49 to 14.98 mg $\cdot$ dm^{-3}, while the content of nitrates was low and medium.

3. The pasture-purpose use of the gyttja soils favoured the process of nitrification and increased washout of nitrates to the groundwaters. It was found out that in the groundwaters in the Mgyhh160ps soils under the pasture the average annual concentration of N-NO_3 amounted to 0.774 mg $\cdot$ dm^{-3} N-NO_3. The highest contents of N-NO_3 in the groundwaters were observed mostly in the summer seasons when the process of nitrification in the soil occurred most intensely.

4. Considering the interdependence between the content of N-NO_3 and N-NH_4 in water in the context of the way of the utilization of the soils, the correlation coefficient for the gyttja soils under the pasture shows a positive correlation for N-NO_3. In the case of the gyttja soils under the birch alder carr there was a similar interdependence as in the soil under the pasture except that only the power of the relation between the content of N-NH_4 in the soil to the concentration in water was statistically significant. In the case of gyttja soils unused and under the meadow, the correlation between the content of nitrogen N-NO_3 in the soil and water was negative.

5. The calculated coefficient of correlation for the gyttja soils irrespective of the way of their use showed that an increase in the concentration of N-NO_3 in the soil involved an increase in the concentration of N-NO_3 in the water. In the case of N-NH_4, in spite of an increase in this form of nitrogen in the soil, a decrease in its concentration in the water was observed.

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MINERALIZACJA ORGANICZNYCH ZWIĄZKÓW AZOTU W GLEBACH GYTIOWO-MURSZOWYCH A ZAWARTOŚĆ AZOTU MINERALNEGO W WODACH GRUNTOWYCH

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Abstrakt: Celem badań było przedstawienie tempa mineralizacji organicznych związków azotu w glebach gytiowo-murszowych położonych w różnych warunkach siedliskowych pojezierza Mrągowskiego i Olsztyńskiego, w okresie wegetacji i podczas zimy. Zbadano stężenia $N\text{-}NO_3$ i $N\text{-}NH_4$ w wodach gruntowych tych gleb i porównano je z dynamiką procesu mineralizacji materii organicznej w glebach. Wyniki badań wykazały, że tempo mineralizacji organicznych związków azotu w badanych glebach było zróżnicowane w poszczególnych porach roku w zależności od stanu ich uwilgotnienia i sposobu użytkowania. Najwięcej azotu mineralnego uwalniało się w glebie gytiowo-murszowej pod pastwiskiem w okresach letnich. W procesie mineralizacji organicznych związków azotu dominowała forma $N\text{-}NO_3$. Użytkowanie pastwiskowe gleb gytiowych sprzyjało procesowi nitryfikacji i zwiększonemu wymywaniu azotanów do wód gruntowych. Stwierdzono, że w wodach gruntowych w glebach Mgyhh160ps pod pastwiskiem, średnie w ciągu roku stężenie $N\text{-}NO_3$ wynosiło 0,774 mg · dm^{-3} $N\text{-}NO_3$. Największe zawartości $N\text{-}NO_3$ w wodach gruntowych stwierdzono przeważnie w okresach letnich, kiedy najintensywniej zachodził proces nitryfikacji w glebie. Wyliczony współczynnik korelacji między zawartością $N\text{-}NO_3$ i $N\text{-}NH_4$ w wodzie i w glebach gytiowych różnie użytkowanych gleb gytiowych pod pastwiskiem ukazuje dodatnią korelację dla $N\text{-}NO_3$. W przypadku gleb gytiowych pod olsem brzozowym były podobne zależności jak w glebie pod pastwiskiem, z tym, że jedynie siła związku między zawartością $N\text{-}NH_4$ w glebie do stężenia w wodzie była istotna statystycznie. W przypadku gleb gytiowych nieużytkowanych i pod łąką korelacja między zawartością azotu $N\text{-}NO_3$ w glebie i wodzie była ujemna. Obliczony współczynnik korelacji dla gleb gytiowych niezależnie od sposobu ich użytkowania wykazał, że ze wzrostem stężenia $N\text{-}NO_3$ w glebie, wzrastało stężenie $N\text{-}NO_3$ w wodzie. W przypadku $N\text{-}NH_4$ pomimo wzrostu tej formy azotu w glebie zaobserwowano spadek stężenia w wodzie.

Słowa kluczowe: mineralizacja, gleby gytiowo-murszowe, warunki siedliskowe, woda gruntowa

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SPATIAL VARIABILITY OF MINERAL NITROGEN FORMS IN SOME SOILS OF POMERANIA AND CUIAVIA REGION

ZMIENNOŚĆ PRZESTRZENNA MINERALNYCH FORM AZOTU W WYBRANYCH TYPACH GLEB REGIONU POMORZA I KUJAW

Abstract: Results concerning spatial variability of mineral nitrogen forms content in the field scale are both of theoretical and practical significance and could be used to optimization of nitrogen fertilization. The objective of this study was to evaluate and compare the spatial variability of mineral nitrogen forms (N-NO_3^- and N-NH_4^+) in the surface horizon (0–20 cm) of two different arable soils: Alfisols and Phaeozems of the Pomerania and Cuiavia region. For this purpose 50 soil samples were taken from each soil type from sampling sites located in a square sampling grid (10 m × 10 m). The results were evaluated with the use of classic statistical and geostatistical methods. Spatial variability of investigated nitrogen forms was evaluated with use of raster maps drawn after the approximation of source data by kriging method applied with the use of the SURFER 8.0 software. The amount of N-NH_4^+ was differentiated both within soil types and between them. Concentration of this nitrogen form in Phaeozems ranged 10.0–28.4 mg · kg^{-1} and was lower than in Alfisols, ranging from 15.9 to 37.1 mg N-NH_4^+ · kg^{-1}. The amount of nitrate nitrogen fluctuated significantly. A higher concentration of this form was noted in Phaeozems (10.6–44.3 mg N-NO_3^- · kg^{-1}) than in Alfisols (6.2 to 51.8 mg N-NO_3^- · kg^{-1}). As confirmed by range values the differentiation of the investigated nitrogen forms within the soil type was very high. It corroborated with coefficients of variations (CV%) for N-NH_4^+ and N-NO_3^- amounting 28.6 and 31.2 in Phaeozems and 22.0 and 48.9 in Alfisols.

Keywords: spatial variability, geostatistics, nitrate(V), ammonium ions

In the literature a lot of attention has been devoted to mineral forms of nitrogen and their transformation in the agricultural space of Poland [1–4]. Very few studies however have concentrated on the spatial variability of those nitrogen forms in the field-scale, what is of a great theoretical and practical significance. Results concerning spatial variability of N-NO_3^- and N-NH_4^+ could be used to nitrogen fertilization optimization. The consequences of forgetting the spatial variability of the soil environment, and thus the conditions of plants growth and development could be irrationalness of tillage

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treatments, higher fertilization expenses and/or a prolonged retention of various compounds in soil or their loss as the consequence of leaching down the profile or volatilisation to the atmosphere [5]. According to nitrogen doses, kind of plants and physicochemical soil properties, plants uptake on the average 50–70 % of N applied as mineral fertilizers [4].

Nitrate nitrogen which is not utilized by plants could be leached down the profile, causing contamination of surface and groundwaters [6]. In turn, too low nitrogen doses, not meeting demand for plants nutritional requirements can reduce the yields and crop quality as well as make worse soil fertility. Since fertilization costs comprise significant contribution in the direct costs structure and fluctuate from 30 to 50 % as dependent on the kind of cultivation [7], optimal method of fertilizers application is also looked for economical purposes. One of them is adjustment of nutrient components doses to potential field productivity results from physicochemical properties especially. Soil spatial variability investigation of both physical and chemical parameters is the basis for the "precision agriculture", which has been strongly promoted and introduced in some areas of the European Union member countries [5].

The objective of this study was to evaluate and compare the spatial variability of mineral nitrogen forms (N-NO_3^- and N-NH_4^+) in the surface horizon of two different cultivated soils of the Pomerania and Cuiavia region, namely Alfisols and Phaeozems [8].

Material and methods

Soils samples were collected from the specified area of a 80-hectare field at the village of Orlinek near Mrocza in the Pomerania and Cuiavia province. Two objects representing a Alfisols and Phaeozems [8] formed from glacial till were chosen since they are typical for that region. The idea of the location was to exclude the influence of other factors on determined soil parameters. Moreover, on both selected areas for some years the same plants have been cultivated and the same agrotechnical treatments are practised. From each soil type 50 soil samples were taken from points located in square sampling grid (10 m × 10 m). Each soil sample accounted for the mean value of 10 individual samplings. The specimens were taken from the surface horizon (0–20 cm) at a stage of the wheat spreading (April 2007). The range of basic parameters of the investigated soils was shown in Table 1.

Table 1

Ranges and means of basic soil physical and chemical parameters

Parameter	Alfisols		Phaeozems	
	Mean	Min. / Max	Mean	Min. / Max
C_{org} [g · kg^{-1}]	7.3	5.5 / 9.0	18.7	13.1 / 25.1
N_{total} [g · kg^{-1}]	0.80	0.68 / 0.99	1.89	1.41 / 3.02
< 0.002 [mm]	6.1	4.0 / 9.0	15.2	7.0 / 20.0
pH in H_2O	5.44*	4.66 / 6.83	7.02*	6.73 / 7.34
pH in 1 M KCl · dm^3	4.70*	4.11 / 5.77	6.78*	6.45 / 7.16

* Geometrical mean.

Nitrate nitrogen content was determined spectrophotometrically, after establishment of colour compound with phenoldisulphonic acid in the anhydrous medium [9] and the ammonium nitrogen was mesured by the indophenol blue method [10]. Basic physico--chemical parameters were determined: pH in H_2O and 1 mol KCl $\cdot$ dm^3 by potentiometric method [11], soil organic C and N content by using a dry combustion CN analyser (Vario Max CN) and particle-size by Cassagrande'a method modyfied by Proszynski [12].

The results were evaluated with the use of classical statistical methods (STATISTICA v. 8.0 Software) calculating arithmetic and geometric means, standard deviation, coefficient of variation as well as skewness and kurtosis. Geostatistical calculations included empirical semivariograms graphs and theoretical mathematical models of variograms. On the basis of the received models the following geostatistic parameters were read out: nugget, sill variance, range of influence and than nugget effects were calculated ([Co/(Co + C)] $\cdot$ 100 [13]. On the ground of semivariograms raster maps illustrating the spatial variance of determined nitrogen forms were drawn. The method of point kriging was adapted to the data estimation [14] and the calculations were done using SURFER 8.0 of Golden Software.

Results and discussion

Mineral nitrogen forms content in the surface horizons of determined soils showed a significant differentiation (Table 2). N-NH_4^+ content in the soil samples taken from surface Alfisols horizon ranged 15.9–37.1 mg N-NH_4^+ $\cdot$ kg^{-1} with mean value 26.5 mg N-NH_4^+ $\cdot$ kg^{-1}. The surface horizon of Phaeozems contained somewhat lower concentration of this nitrogen form (10.0–28.4 mg $\cdot$ kg^{-1}), amounting to 14.7 mg N-NH_4^+ $\cdot$ kg^{-1}. Ammonium nitrogen content determined in both soil types occurred in the ranged of values obtained by Spychaj-Fabisiak and Murawska [15] in the surface area of the Pomerania and Cuiavia region soils. Statistical analysis showed that ammonium nitrogen content in the most of Alfisols samples was higher than the mean value, what was indicated by a higher median than the mean value (27.7 mg N-NH_4^+ $\cdot$ kg^{-1}) as well as the negative value of skewness showing left-sided asymmetry. However, the majority of Phaeozems samples contained less N-NH_4^+ than the mean value, what was evidenced by a lower median than the mean and positive skewness (Table 2). Excepting differentiation between the compared soil types results revealed a high changeability of N-NH_4^+ within the same soil type. A greater variability of N-NH_4^+ was noted for Alfisols, what was confirmed by higher standard deviation values than for Phaeozems and negative kurtosis values (–0.73), giving the evidence of flattened distribution (Table 2).

Geostatistical analysis (Table 2) showed that NH_4^+ ions in Alfisols surface level occurred in a smaller dispersion than in the same level of Phaeozems. It was confirmed by higher values of nugget variance occurring on the semivariogram drawn for Alfisols (4.79 (mg $\cdot$ $kg^{-1})^2$), as compared with the one done for Phaeozems (0.28 (mg $\cdot$ $kg^{-1})^2$). This fact could indicate a short-range variability. A higher changeability of this parameter in Alfisols was confirmed by a higher sill variance (31.79 (mg $\cdot$ $kg^{-1})^2$), than

Table 2

Basic statistical and geostatistical parameters of ammonium (N-NH_4^+) and nitrate (N-NO_3^-) nitrogen under study [mg · kg^{-1}]

Parameter	Alfisols		Phaeozems	
	NH_4^+	NO_3^-	NH_4^+	NO_3^-
n	50	50	50	50
Minimum	15.9	6.8	10.0	10.6
Maximum	37.1	51.8	28.4	44.3
Arithmetical mean	26.5	15.6	14.7	22.8
Geometrical mean	25.8	14.3	14.2	21.8
SD*	5.9	7.6	4.2	7.1
Median	27.7	13.7	13.2	21.3
CV [%]**	22.0	48.9	28.6	31.2
Kurtosis	–0.73	9.60	1.63	0.71
Skewness	–0.44	2.56	1.43	0.92
Model	Spherical, Linear	Spherical	Spherical, Linear	Spherical, Linear
Nugget (Co)	4.79	5.78	0.28	3.35
Sill (Co+C)	31.79	43.8	10.55	31.63
[Co/(Co+C)] · 100	15.1	13.2	2.7	10.6
Range [m]	77.4	16.6	17.53	11.33

* SD – standard deviation; ** CV [%] – coefficient of variation.

that calculated for the Phaeozems samples (Table 2, Fig. 1a, 1b). In the most cases the variability had a structural character, what was indicated by low nugget effects.

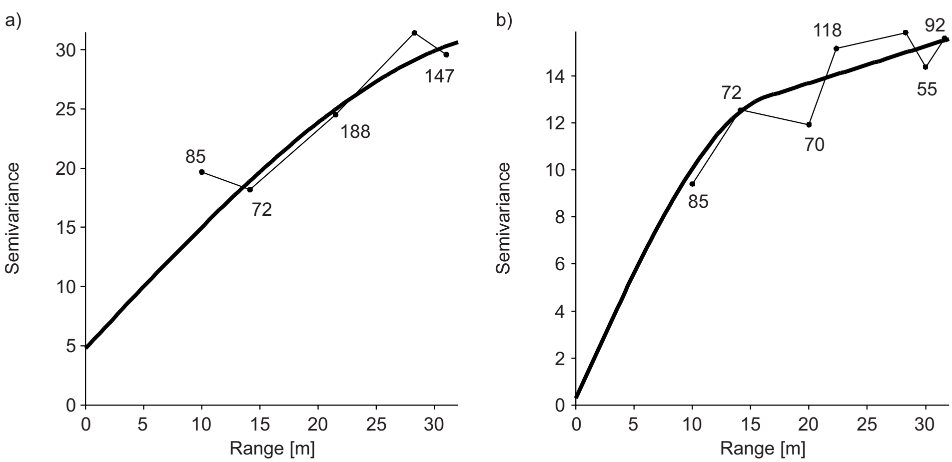

Fig. 1. Empirical semivariograms of NH_4^+ ions in the surface horizon of Alfisols (a), and Phaeozems (b) with estimated theoretical models

For display of N-NH_4^+ content variability, raster maps calculated on the basis of semivariograms in both investigated soils were drawn (Figs. 2, 3). They show that the most of Alfisols surface horizon ranged 20–30 mg N-NH_4^+ · kg^{-1} and amounts < 20 and > 35 mg N-NH_4^+ · kg^{-1} had the point character. However, the most of Phaeozems investigated area the ammonium nitrogen content ranged less than 20 mg N-NH_4^+ · kg^{-1}.

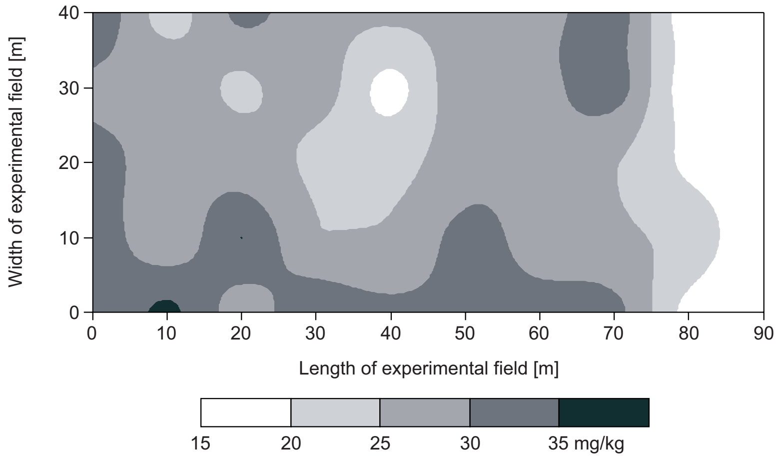

Fig. 2. Spatial variability of NH_4^+ ions in the surface horizon of Alfisols

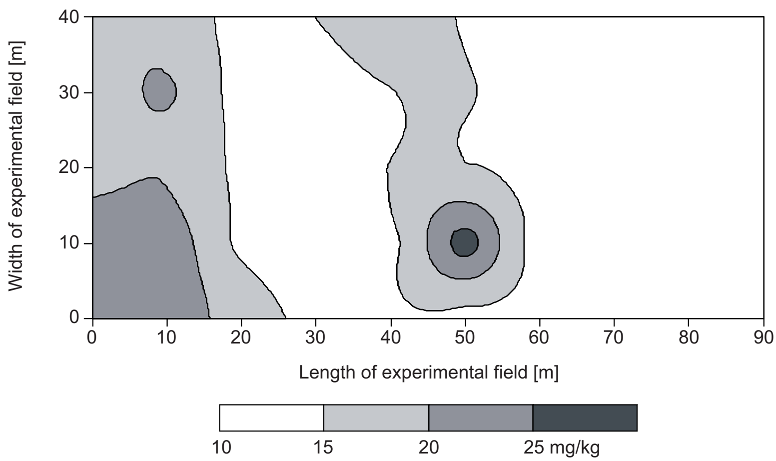

Fig. 3. Spatial variability of NH_4^+ ions in the surface horizon of Phaeozems

The analysis of nitrate nitrogen, the second mineral nitrogen form, showed a greater spatial variability in the surface horizons of the investigated soils than ammonium concentration, what indicated an extensive range of its concentrations in both Alfisols and Phaeozems (Table 2). The wider range of N-NO_3^- was characteristic for Alfisols surface horizon (6.8–51.8 mg N-NO_3^- · kg^{-1}), while their concentration in Phaeozems ranged 10.6–44.3 mg N-NO_3^- · kg^{-1}. The N-NO_3^- content recorded in this case was in the range of results obtained by Spychaj-Fabisiak and Murawska [15] for soils of the Pomerania and Cuiavia region, whereas the mean value for the investigated soil samples was higher than for the whole region (15.6 mg N-NO_3^- · kg^{-1}). A higher N-NO_3^- variability, as compared with the N-NH_4^+ changeability was confirmed by higher variation coefficients obtained for this form (Table 2). In spite of a wider range of nitrate nitrogen in the Alfisols surface horizon (0–20 cm) it showed a higher concentration than in Phaeozems, what was confirmed by a higher kurtosis value (9.6) than the one found for Phaeozems (0.71).

Most soil samples of both Alfisols and Phaeozems surface horizons contained lower amounts of N-NO_3^- as compared with mean values, what was confirmed by a lower median than mean values as well as by positive values of kurtosis indicating a right-sided skewness (Table 2). The distribution of N-NO_3^- contents in both investigated soils was of a different character in comparison with the results distribution (skewness and kurtisis negative) reported by Stenger et al [16] for Alfisols formed from loess.

Despite of a very wide N-NO_3^- concentration range in the surface horizons of the investigated soils, confirmed also by the sill variance ranging 43.8 (mg · $kg^{-1})^2$ in Alfisols and 31.63 (mg · $kg^{-1})^2$ in Phaeozems, this form of nitrogen is usually localised in soil in some clusters, which are smaller than the distance of the range of sampling. The confirmation of short-range variability occurrence came from the analysis of the nugget values amounting 5.78 (mg · $kg^{-1})^2$ for Alfisols and 3.35 (mg · $kg^{-1})^2$ for Phaeozems (Table 2, Fig. 4a, 4b).

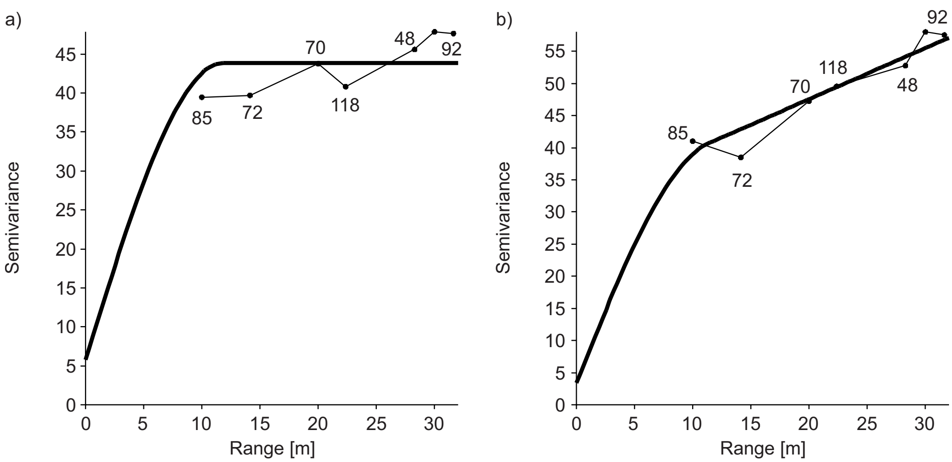

Fig. 4. Empirical semivariograms of NO_3^- ions in the surface horizon of Alfisols (a) and Phaeozems (b) with estimated theoretical models

However, contribution of this kind of variability in total changeability is not large. It was illustrated by nugget, what indicated the participation of nugget variance in the total sill variance (Table 2). A similar nugget effect values was reported by Stenger et al [16], whereas a higher nugget effect was noted by Cambardella et al [17] in soils of Iowa.

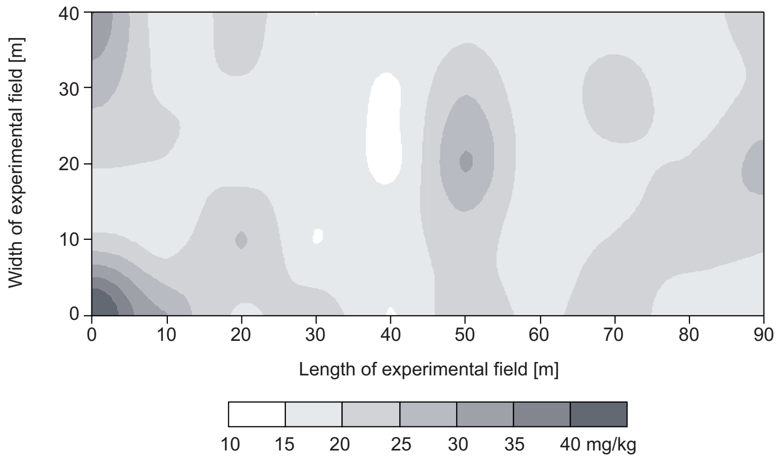

Fig. 5. Spatial variability of NO_3^- ions in the surface horizon of Alfisols

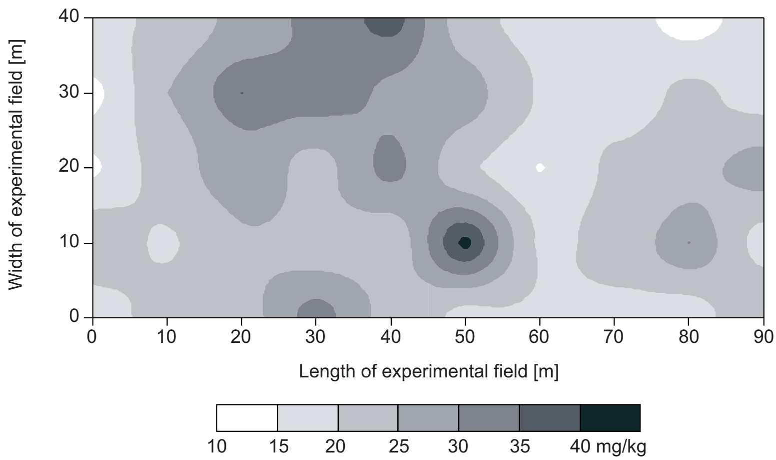

Fig. 6. Spatial variability of NO_3^- ions in the surface horizon of Phaeozems

Similarly, the raster maps drawn on the basis of semivariograms showed a smaller spatial variability of N-NO_3^- concentration in the surface horizon of Alfisols, than in Phaeozems because a bigger area of this soil contained N-NO_3^- in the range 10–25 N-NO_3^- · kg^{-1} (Figs. 5, 6). The range of influence calculated for both forms of mineral nitrogen, defined as a maximum distance of correlations between point values, showed that the distance of soil sampling for both N-NH_4^+ and N-NO_3^- contents determination should not be no more than 10 m, since this is the highest distance where point results of N-NH_4^+ and N-NO_3^- concentration could be autocorrelated (Table 2, Fig. 1a, 1b, 4a, 4b).

Conclusions

1. The analysis showed differentiation of the spatial variability of ammonium and nitrate nitrogen concentrations in the surface horizons of the Alfisols under study. A higher variability of the determined nitrogen forms was characteristic for Alfisols, in spite of a lower organic carbon and clay fraction differentiation.

2. A higher spatial variability within the soil type showed $N\text{-}NO_3^-$ concentration as compared with the amounts of $N\text{-}NH_4^+$, what could indicate a high variability of soil solution within the surface horizon.

3. The soils under study differentiated not only in the concentration of analyzed nitrogen forms but also in their distribution, what was confirmed by the varied values of skewness and kurtosis. A possible cause of this observation could be differentiation of basic parameters of surface horizon within the given soil type.

4. The comparison of $N\text{-}NH_4^+$ and $N\text{-}NO_3^-$ amounts in the analysed soil horizon showed discrimination between both soils under study. Average $N\text{-}NH_4^+$ content was higher in the surface horizon of Alfisols, while the amounts of $N\text{-}NO_3^-$ were more concentrated in the surface layer of Phaeozems.

Acknowledgements

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ZMIENNOŚĆ PRZESTRZENNA MINERALNYCH FORM AZOTU W WYBRANYCH TYPACH GLEB REGIONU POMORZA I KUJAW

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Abstrakt: Wyniki badań dotyczących zmienności przestrzennej zawartości mineralnych form azotu w skali pola uprawnego mogą mieć znaczenie zarówno poznawcze, jak i praktyczne i mogą być wykorzytane do optymalizacji nawożenia roślin azotem. Celem badań było rozpoznanie i porównanie zmienności przestrzennej zawartości mineralnych form azotu ($N\text{-}NO_3^-$ oraz $N\text{-}NH_4^+$) w poziomie powierzchniowym dwóch odmiennych typów gleb uprawnych obszaru Pomorza i Kujaw, a mianowicie gleba płowa oraz czarna ziemia. W tym celu z każdego typu gleby pobrano 50 próbek z punktów zlokalizowanych w sztywnej siatce kwadratów o boku 10 m. Otrzymane wyniki opracowano metodami statystycznymi i geostatystycznymi. Zmienność przestrzenną badanych form azotu określono na podstawie map rastrowych wykreślonych po aproksymacji danych źródłowych metodą krigingu. Zawartość $N\text{-}NH_4^+$ była zróżnicowana zarówno w badanych typach gleb, jak i pomiędzy nimi. Zawartość tej formy azotu w czarnej ziemi mieściła się w zakresie 10.0–28.4 mg $\cdot$ kg^{-1} i była mniejsza niż w glebie płowej, która zawierała od 15.9 do 37.1 mg $N\text{-}NH_4^+ \cdot kg^{-1}$. Odmiennie kształtowała się natomiast zawartość formy azotanowej, której większe ilości stwierdzono w czarnej ziemi (10.6–44.3 mg $N\text{-}NO_3^- \cdot kg^{-1}$) niż w glebie płowej, która zawierała od 6.8 do 51.8 mg $N\text{-}NO_3^- \cdot kg^{-1}$. Jak wynika z przedstawionych zakresów, zróżnicowanie zawartości badanych form azotu w obrębie typu gleby było również bardzo duże. Potwierdzają to obliczone współczynniki zmienności (CV%) dla $N\text{-}NH_4^+$ i $N\text{-}NO_3^-$ wynoszące odpowiednio: 28.6 i 31.2 w czarnej ziemi oraz 22.0 i 48.9 w glebie płowej.

Słowa kluczowe: zmienność przestrzenna, geostatystyka, azotany(V), jony amonowe

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and Janusz POSŁUSZNY[2]

EFFECT OF MUNICIPAL LANDFILL LEACHATE ON THE CONTENT OF NITROGEN FORMS IN UNDERGROUND AND SURFACE WATERS

WPŁYW ODCIEKÓW ZE SKŁADOWISKA ODPADÓW KOMUNALNYCH NA ZAWARTOŚĆ FORM AZOTU W WODACH PODZIEMNYCH I POWIERZCHNIOWYCH

Abstract: The study has been carried out on the grounds of a municipal landfill in Brodnica. Water samples were collected from 6 sites in different locations. It has been demonstrated that the values of total nitrogen concentrations as well as mineral forms of this element in leachates, ground and surface water were highly varied. In the landfill leachate, the total nitrogen content reached 216.7 mg N dm^{-3}, of which 91.6 % consisted of ammonia nitrogen, 2.9 % was nitrate(V) nitrogen and 0.08 % was nitrate(III) nitrogen.

The quality of deep groundwater sampled from an observation borehole drilled on a site where groundwater flows towards the landfill basin corresponded to water purity class I, but fell to class V for groundwater collected from a piezometer situated behind the landfill basin, where the water flows away from it. The total nitrogen and mineral nitrogen forms in groundwater depended on a sampling site. Further away from the landfill cap, concentrations of total and ammonia nitrogen were lower. Considering the above parameters, the quality of groundwater sampled from a piezometer closer to the landfill was within class V, but water samples taken from a piezometer situated further away from the landfill were assigned class II or III. No negative influence of the landfill on the quality of surface waters has been observed as over 94 % of the determinations of biogenic substances did not exceed the threshold values established for water purity class I.

Keywords: landfill, forms of nitrogen, groundwater, surface water

One of the most serious problems caused by building and operating a municipal waste landfill is the migration of leachete to ground, surface and even confined groundwater. Leachate appears as a result of rainwater seeping downwards through the landfill. A much smaller amount of leachate originates from liquids brought to the landfill with waste or derived from the breakdown of organic matter. In some cases,

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increased quantities of leachate can be attributed to surface and groundwater reaching the landfill [1–7].

Most landfills in Poland are inadequately located and operated. Frequently, the hydrogeological or geotechnical conditions of the sites where landfills were created had not been tested, which means that under a certain combination of hydrogeological conditions migration of leachate in water bearing soil layers may take place over considerable distances unless adequate prevention measures are place.

The aim of this study has been to analyze the potential hazard caused by leachate occurring at an active municipal landfill, which can penetrate the water and soil environment. This paper presents the effects of leachate on pollution of ground and surface waters with nitrogen compounds.

Material and methods

The study has been performed on the grounds of an active municipal water landfill in Brodnica, which belongs to the Przedsiebiorstwo Gospodarki Komunalnej sp. z o.o. (Municipal Services Company Ltd.). The landfill is located 350 m off the Drweca River and 900 m away from the secondary protection zone of a municipal water intake point. To the north, the landfill grounds border with a wastewater treatment plant and west of the landfill there is an animal asylum. There are screens isolating the landfill cap from the groundwater and limiting the migration of pollutants in soil, which have been constructed to control the negative influence of the landfill on environment [8].

In order to determine the effect of leachate on the quality of underground (ground and deep ground) and surface water, measurements of the water table were made along with the physicochemical assays of the leachate and water. Water samples for analyses were taken according to the Polish norms: PN-ISO 5667-11:2004; PN-76/C-04620 and PN-88/C-04632. The samples were collected once every four months from six points set at different locations. The sampled water was tested for the total nitrogen content, ammonia nitrogen ($N\text{-}NH_4$), nitrate(V) nitrogen ($N\text{-}NO_3$) and nitrate(III) nitrogen ($N\text{-}NO_2$). The laboratory analyses were made according to the analytical protocols contained in the Polish norms (PN-82/C-04576).

The samples of leachate were collected from the pump station located behind the landfill basin. Samples of groundwater were taken from four piezometers situated around the landfill basin. Confined groundwater was sampled from piezometer P1 (a model observation borehole for determination the hydrochemical background), drilled on a site where groundwater flows towards the landfill, and from piezometer P2, situated where water flows away from the dump. Samples of groundwater were taken from piezometer P3, which was located near a narrow-gauge rail embankment and from piezometer P4, about 8 meters away from the leachate pump station. Both piezometers were drilled on sites where water flows away from the landfill.

The results were processed statistically using the software programme Statistica version 6 (StatSoft Inc. 2001). The least significant differences (LSD) were determined at the level of significance $p = 0.05$.

The evaluation of the quality of water has been made according to the criteria specified in an appendix to the Ordinance of the Minister for Environment of 11th February 2004 on the classification for presentation of the state of surface and groundwater, methods for monitoring water, interpretation of the results and presentation of the state of water (Journal of Laws, No. 32, item 284) [9] and Ordinance of the Minister of the Environment of 14th July 2006 on execution of duties laid on industrial sewage suppliers and conditions for disposal of sewage to sewage facilities (Journal of Law, No. 136, items 963 and 964) [10].

Results and discussion

Many authors [1, 3–5, 7, 11–14] report that effluents from municipal landfills are highly varied in their characteristics. The chemical composition of leachate as well as its amount depend on the age of a landfill, waste disposal technologies, type and fragmentation of waste, amount of water infiltrating cells of waste and methods applied for land reclamation.

Total, nitrate(V), nitrate(III) and ammonia nitrogen are perceived as biogenic parameters in the light of the Ordinance of the Minister for Environment of 11th February 2004 [9]. Many authors [2, 6, 15–17] suggest that the concentration of nitrogen and its mineral forms in landfill leachate is typically high and varies in time.

In Poland, most active landfills are stabilized and therefore the leachate originating from such landfills possesses small levels of organic compounds but very high concentrations of nitrogen compounds.

The leachate management is one of the most difficult tasks that the Municipal Services Company in Brodnica has to deal with. The reason is that the leachate from the landfill in Brodnica contains a very high load of pollutants whereas the quality requirements imposed on treated wastewater are extremely strict.

In the analyzed leachate, the concentrations of biogenic parameters such as the total nitrogen and mineral forms of nitrogen were much lower compared with leachate from other landfills operated for comparably long periods of time [18–22].

The average concentration of total nitrogen reached 216.70 mg N dm^{-3}, of which 91.6 % consisted of ammonia nitrogen (Fig. 1). The highest total nitrogen content was

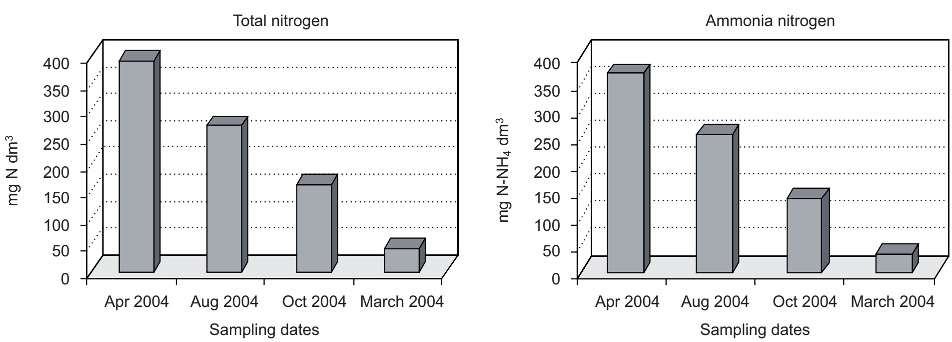

Fig. 1. Total and ammonia nitrogen concentrations in landfill leachate

determined in June 2004, and the lowest occurred in March 2005. Statistical differences in the concentrations of total nitrogen between the sampling dates proved to be highly significant (Table 1). During our study, the total nitrogen concentration decreased considerably, from 392.16 to 42.33 mg N dm^{-3}, which could be attributed to the extensive dilution of leachate that took place when the landfill zone II was connected to a system of draining pipes. Another reason was denitrification occurring in the landfill.

Table 1

Statistical calculations for nitrogen forms

Parameter Indices	$LSD_{0.05}$	Standard deviation	Standard error
Leachate			
Total nitrogen	19.46	149.55	74.77
Ammonia nitrogen	19.15	144.86	72.43
Nitrate(V) nitrogen	3.52	4.90	2.45
Nitrate(III) nitrogen	0.41	0.07	0.03
Groundwater			
Total nitrogen	6.65	12.68	6.55
Ammonia nitrogen	1.83	1.41	0.70
Nitrate(V) nitrogen	6.42	9.09	6.04
Nitrate(III) nitrogen	0.24	0.01	0.01
Deep groundwater			
Total nitrogen	4.47	4.72	2.50
Ammonia nitrogen	1.90	1.56	0.79
Nitrate(V) nitrogen	0.57	0.09	0.05
Nitrate(III) nitrogen	0.25	0.02	0.01
Surface water			
Total nitrogen	3.11	6.28	0.99
Ammonia nitrogen	1.70	1.99	0.12
Nitrate(V) nitrogen	0.47	0.10	0.03
Nitrate(III) nitrogen	0.18	0.01	0.01

Several researchers [2, 3, 16, 23] reported that among the mineral forms of nitrogen, the highest contribution to total nitrogen is made by ammonia nitrogen, which in leachate from stabilized landfills can reach over 2.000 mg $N\text{-}NH_4$ dm^{-3}. On new landfills, such a high concentration of ammonia nitrogen is caused mainly by the presence of organic acids, which inhibit nitrification. In turn, ammonia nitrogen in leachate from stabilized landfills originates predominantly from processes of hydrolysis and fermentation of biodegradable organic compounds, which contain proteins.

In the leachate analyzed an external laboratory, there were highly significant differences in values of ammonia nitrogen (Fig. 1, Table 1). The average concentration of this nitrogen form reached 198.40 mg $N\text{-}NH_4$ dm^{-3}. Analogously to total nitrogen, the concentration of ammonia nitrogen, which ranged between 368.55–33.85 mg N-NH_4 dm^{-3}, fell drastically over the study period. The highest level of ammonia nitrogen occurred in June 2004 and the lowest – in March 2005.

The average concentration of nitrate(V) nitrogen in the landfill leachate sampled from a collecting well was small (5.69 mg N-NO_3 dm^{-3}) but, like total and ammonia nitrogen, highly variable (0.67–11.48 mg N-NO_3 dm^{-3}) (Fig. 2, Table 1). Differences in the concentrations of nitrate(V) nitrogen determined between the leachate collected in August 2004 and March 2005 were non-significant, whereas those between the other sampling dates proved to be statistically significant. The highest concentration of nitrates(V) was observed in June and the lowest in August 2004.

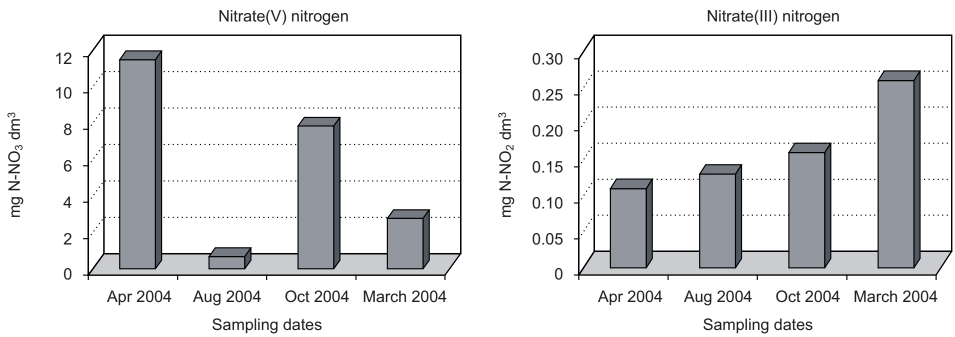

Fig. 2. Nitrate(V) and nitrate(III) nitrogen concentrations in landfill leachate

Our analysis of the fluctuations of nitrate(III) nitrogen shows that the concentration of this nitrogen form continued to increase considerably in time, which indicates that nitrification was at play (Fig. 2). The concentration of ammonia nitrogen over the whole time period decreased largely and eventually fell down to 33.85 mg N-NH_4 dm^{-3}.

The influence of a landfill on natural environment can be examined by testing concentrations of pollutants in ground and surface water. The extent of such an influence is measured as a distance from the landfill cap to the line around the landfill where the determined values of pollutants equal those characteristic of the hydrogeochemical background [24–27].

Suchy et al [5] report that waste landfills are usually situated over the surface or close to the surface of the earth, which means they enter the natural water circulation system. Atmospheric precipitations penetrate from the surface land into the landfill masses and seep through the dumped waste, transporting leached pollutants to groundwaters. In Poland, an average 1.000 m^3 of water passes through 1 ha of land each year (100 mm/year).

The scale of pollution caused by leachate migrating to ground and surface water can be assessed by observing the quality of water via a network of boreholes (piezometers) or through assays of water in wells near a given landfill [5, 15, 23, 28].

During our investigations, the deep groundwater samples from model piezometer P1 situated outside the landfill basin, where water flows towards the landfill, showed a significant increase in total nitrogen, which was within the range of 0.47–11.04 mg N

dm^{-3} (Fig. 3, Table 1). Such quantities of nitrogen correspond to water purity class IV. The highest values occurred in March 2005 and the lowest – in August 2004. The differences between the values of the total nitrogen content in water sampled in October 2004 and in August 2004 or March 2005 were non-significant, unlike the differences between the determinations obtained in water samples collected in August 2004 and March 2005, which were highly significant. High concentrations of total nitrogen in water collected from the model piezometer are not a measure of the quality of waters originating from the landfill, but imply pollution from other sources in the area where the borehole was drilled.

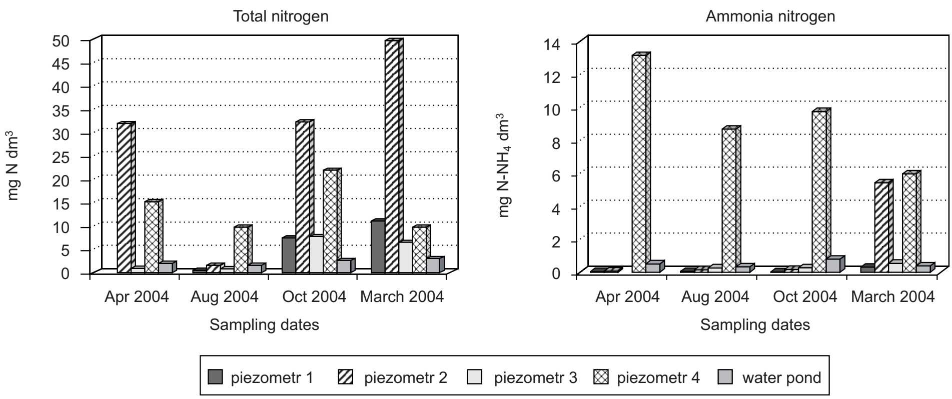

Fig. 3. Total nitrogen and ammonia nitrogen concentration in ground and surface water

The confined groundwater sampled from piezometer P2, located to capture water flowing away from the landfill, was classified as water purity class V according to the total nitrogen content. However, it cannot be stated firmly that such poor quality of water is caused solely by the proximity to the landfill. Several assays imply contamination from other local sources (the animal asylum). Besides, among the parameters most highly exceeded at this site there are the ones which were determined to be much lower in groundwater collected from a piezometer on the landfill itself.

The average value of the total nitrogen concentration in groundwater sampled from piezometer P3, located behind the narrow-gauge rail embankment was 4.99 mg N dm^{-3}, which is assigned to water purity class III, whereas in the water samples obtained from piezometer P4, located behind the landfill basin, the analogous determination equalled to 14.13 mg N dm^3, which allocated the water to class V. In the former case, the highest values of total nitrogen were observed in March 2005, and the lowest ones occurred in August 2004. In the latter case, the highest total nitrogen content appeared in October 2004, dropping to its lowest level in August 2004 and March 2005.

The value of total nitrogen in surface water collected from a water pond ranged around 2.30 mg N dm^{-3} and that of ammonia nitrogen was at a level of 0.50 mg $N\text{-}NH_4$ dm^{-3}, which means that the pond water belonged to water purity class I (Fig. 3). The concentrations of nitrate(V) and nitrate(III) nitrogen were likewise low (Fig. 4).

The level of ammonia nitrogen in deep groundwater collected from model piezometer P1 ranged between 0.02–0.31 mg $N\text{-}NH_4$ dm^{-3}, which corresponds to water purity class I (Fig. 3, Table 1). Much higher concentrations of this form of nitrogen were determined in deep groundwater collected from piezometer P2, located on the animal asylum grounds, where the highest values were recorded in March 2005 and the lowest ones appeared in June 2004. An evident increase in the ammonia nitrogen concentration, which ranged within 0.08–5.43 mg $N\text{-}NH_4$ dm^{-3}, was found. The average value of the concentration of this nitrogen form was 1.46 mg $N\text{-}NH_4$ dm^{-3}, which allocates the tested water to class V. The above suggests that confined groundwater sampled around the landfill does not meet the requirements set for potable and household use waters. The parameter which disqualifies them in that case is the amount of ammonia (over 2-fold above the threshold).

In the groundwater sampled from piezometer P3, the average value of ammonia nitrogen was 0.36 mg $N\text{-}NH_4$ dm^{-3}, which classify this water to water purity class II. In the groundwater taken from piezometer P4, the analogous value was 9.39 mg $N\text{-}NH_4$ dm^{-3}, meaning that it belonged to class V. In both cases, the highest values were determined in March 2005 and the lowest ones – in August 2004. The high values of ammonia concentrations noticed in observation well P4 suggest the reducing character of the process occurring in the local groundwater.

The concentration of nitrate(V) nitrogen in deep groundwater collected from piezometers P1 and P2 was within the range of 0.36–43.95 mg $N\text{-}NO_3$ dm^{-3} (Fig. 4, Table 1). The average value of this nitrogen form in water collected from model piezometer P1 was 6.03 mg $N\text{-}NO_3$ dm^{-3}, which allocated it to class II. In the water sampled from piezometer P2 the determined value was 26.99 mg $N\text{-}NO_3$ dm^{-3}, which makes it belong to class V. In the water sampled from piezometer P1, the highest values were recorded in March 2005 and the lowest ones in August 2004. A reverse situation occurred in the case of water collected from piezometer P2.

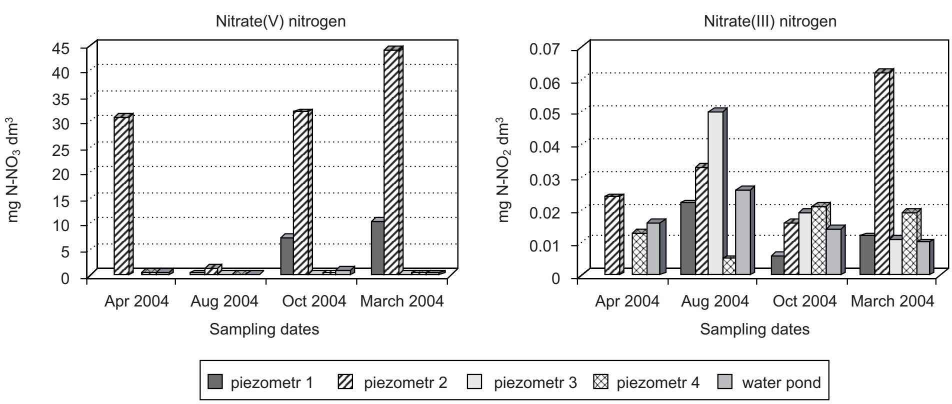

Fig. 4. Nitrate(V) and nitrate(III) nitrogen concentration in ground and surface water

The groundwater sampled from piezometer P3 showed variation in the content of nitrate(V) nitrogen, ranging from 0.06 to 0.15 mg $N\text{-}NO_3$ dm^{-3}. In the water obtained from piezometer P4, the analogous determinations varied from 0.24 to 0.54 mg N-NO_3 dm^{-3}. Such values enabled assigning water purity class I. In both cases, the differences in the content of nitrate(V) nitrogen between the sampling dates proved to be non-significant.

The concentration of nitrate(III) nitrogen found in the groundwater collected from model piezometer classify it as belonging to class I. Its level in the deep groundwater sampled from piezometer P2 allocated it to class II (Fig. 4). No significant differences in the concentrations of nitrate(III) nitrogen between the sampling dates occurred at either of the piezometers.

In the groundwater collected from piezometer P3, the average concentration of nitrate(III) nitrogen was 0.027 mg N-NO_2 dm^{-3}, which is a value ascribed to water purity class II. In the water collected from piezometer P4, the analogous value was even lower, 0.0145 mg N-NO_2 dm^{-3}, which corresponds to water purity class I. The highest levels of nitrate(III) nitrogen were observed in October and the lowest – in August 2004.

Conclusions

1. The analyzed leachate contained, on average, 216.7 mg N dm^{-3}, of which 91.6 % consisted of ammonia nitrogen, 2.9 % was made up of nitrate(V) nitrogen and 0.08 % was nitrate(III) nitrogen.
2. The quality of deep groundwater collected from a piezometer drilled on a site where water flows towards the landfill basin corresponded to water purity class I. However, the water samples collected from a piezometer catching water flowing away from the landfill proved to belong to class V.
3. The concentration of total nitrogen and its mineral forms in groundwater depended on a sampling site. The further from the landfill cap, the lower the concentrations of total and ammonia nitrogen. Considering these as water quality parameters, the groundwater sampled from a piezometer closer to the landfill was allocated to class V, whereas the samples taken from a piezometer further away from the dump were belonged to water purity class II or III.
4. The landfill in Brodnica does not have an adverse effect on the quality of surface water, as over 94 % of the determinations of biogenic parameters did not exceed the threshold levels established for water purity class I (very good water quality).

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WPŁYW ODCIEKÓW ZE SKŁADOWISKA ODPADÓW KOMUNALNYCH NA ZAWARTOŚĆ FORM AZOTU W WODACH POWIERZCHNIOWYCH I PODZIEMNYCH

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Abstrakt: Badania przeprowadzono na terenie składowiska odpadów komunalnych w Brodnicy. Próbki wód pobierano z 6 różnie usytuowanych punktów. Wykazano, że wartości stężeń azotu ogółem oraz mineralnych form tego składnika w odciekach, wodach podziemnych i powierzchniowych były bardzo zróżnicowane. W odciekach składowiskowych średnia wartość stężenia azotu ogółem kształtowała się na poziomie 216.7 mg N dm^{-3}, z czego 91.6 % stanowił azot amonowy, 2.9 % azot azotanowy(V) oraz 0.08 % azot azotanowy(III). Jakość wód wgłębnych pobieranych z otworu obserwacyjnego usytuowanego od strony napływu wód podziemnych w kierunku niecki składowiska odpowiadała I klasie jakości wód, natomiast pobieranych z piezometru usytuowanego za niecką składowiska na kierunku odpływu wód ze składowiska – V klasie. Wartość stężenia azotu ogółem i jego mineralnych form w wodach gruntowych była uzależniona od miejsca pobierania próbek. Im dalej od czaszy składowiska, tym wartości stężenia azotu ogółem i amonowego były mniejsze. Biorąc pod uwagę wymienione parametry, jakość wód gruntowych pobieranych z piezometru usytuowanego bliżej składowiska odpowiadała V klasie, natomiast pobieranych z piezometru położonego w dalszej odległości od składowiska – II lub III klasie. Nie stwierdzono negatywnego oddziaływania składowiska odpadów na jakość wód powierzchniowych, bowiem ponad 94 % oznaczeń wskaźników biogennych nie przekroczyło wartości granicznych dla I klasy jakości wód.

Słowa kluczowe: składowisko odpadów, formy azotu, odcieki, wody podziemne i powierzchniowe

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and Urszula PISZCZ[1]

EFFECT OF NITROGEN FORM AND DOSE ON NITRATES(V) CONTENT IN SELECTED SPECIES OF VEGETABLES

WPŁYW DAWKI I FORMY AZOTU NA ZAWARTOŚĆ AZOTANÓW(V) W WYBRANYCH GATUNKACH WARZYW

Abstract: The aim of this work was the assessment of the effect of increasing doses of different forms of nitrogen nitrates(V) accumulation in lettuce and radish roots. Research was carried out on the basis of exact cultivation experiments conducted in the years 2003–2005 in a cold greenhouse. The two plant species were fertilized in each year of the experiment, in spring and autumn, with following doses of nitrogen 0.5; 1.0; 1.5; 2.0; and 3.0 g N · pot^{-1} , introducing nitrogen in the forms of $(NH_4)_2SO_4$, $Ca(NO_3)_2$, NH_4NO_3 and $CO(NH_2)$. Investigation was conducted on light soil of slightly acid reaction, featuring the following contents of chemical elements: low-potassium, medium-phosphorus and high-magnesium. The effect of nitrogen form and dose was assessed through analysis of yield size of cultivated plants, total nitrogen and nitrates(V) content. After investigation had been finished, there was determined the content of mineral nitrogen in soils. The research proved that both lettuce and radish yields increased according to gradually increasing dose of nitrogen, up to 1.5 g N · pot^{-1}. The most intensive yield–forming effect in the case of lettuce showed calcium saltpetre, while for radish it was ammonium saltpetre. Significantly higher yields of both plants originating from the same treatments were obtained from spring cultivation. The highest concentration of nitrate(V) nitrogen was assayed in both plants when fertilization with the highest nitrogen dose, yet it was always lettuce to contain higher amounts of this element than radish. Lower quantities of nitrates(V) in each of the examined species were recorded in the spring, while in the autumn these values were higher. Regardless the species, the highest amount of nitrates(V) were accumulated in plants fertilized with calcium and ammonium saltpetre, while the lowest quantities were obtained for application of ammonium sulfate.

Keywords: nitrogen fertilization, forms of nitrogen, nitrate(V) nitrogen, term of cultivation, lettuce, radish

Among a number of cultivation technology factors nitrogen fertilization features the most profound effect on nitrates(V) accumulation in plants. It was reported [1, 2], that under the influence of increasing fertilization with selected forms of nitrogen there occurs increased uptake of this element by plants, but nitrogen usability for protein

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synthesis becomes gradually less efficient. As a result a considerable increase in nitrate(V) fraction contribution to total nitrogen becomes a fact. Apart from the dose of nitrogen fertilizer, the very form of nitrogen, contained in the fertilizer in question, significantly effects on nitrates(V) accumulation. It was proved that the most considerable effect on accumulation of this nitrogen form in plant tissues characterizes fertilization with saltpetre form of nitrogen. The latter one is of a quick effect and nitrate(V) ion, not stored in soil, is quickly absorbed by plants. When nitrogen is applied in the form of ammonium, nitrogen uptake is markedly lower as it depends on nitrification process, as well as the pace of releasing nitrate(V) ions to soil solution [3–5]. Numerous authors also agree that the length of plant growing period and light conditions do considerably effect on nitrates(V) concentration in plants. The highest concentrations are detected in early stages of plant development, and generally, as the plant growing period went by, nitrates(V) content decreases [6–9]. An important role in nitrates(V) accumulation is also played by the term of cultivation and nitrates(V) content, is the highest in winter and early spring, while the lowest values were recorded in late autumn and in the summer, which is connected with intensity of daylight and photosynthesis and results in nitrates(V) reduction [10–12].

Material and methods

Research was conducted on the basis of exact cultivation – pot experiment carried out in years 2003–2005. Investigation was conducted on a light soil of slightly acid reaction, featuring the following contents of chemical elements: low-potassium, medium-phosphorus and high-magnesium. In order to provide proper conditions for plants grow and development basic mineral fertilization for pot experiments was applied. Seeds of lettuce and radish were sow in prepared soil and each experimental object was cultivated in 4 replications. After germination in every pot 8 plants were left. Nitrogen was applied as $(NH_4)_2SO_4$, $Ca(NO_3)_2$, NH_4NO_3 and $CO(NH_2)$ in increasing doses 0.5; 1.0; 1.5; 2.0; and 3.0 g N $\cdot$ pot^{-1}. All the nitrogen doses were divided – one half was applied before sawing and the second half in two doses was applied during vegetation. The two plant species were cultivated in each year of the experiment, in the spring and in the autumn. During the vegetation period soil humidity and plant health were controlled. Ripe plants were collected and mass of yield as well as content of nitrogen(V) by xylenol method were determined. After completing the investigation soil samples from pots were collected and total nitrogen content by Kiejdahl method, as well as nitrate(V) and ammonium nitrogen were determined. Both forms were measured by colorimeters – nitrate(V) nitrogen with diphenylosulfone acid and ammonium nitrogen with Nessler's reagent.

Results and discussion

Nitrogen fertilization contributed to a significant increase in yield size of lettuce and radish, as compared with control treatment, when this component was applied up to the dose of 1.5 g N per pot Table 1. At higher doses in each case there was observed evident, significant yield size reduction of both plants, which speaks for the fact that in order to obtain maximum yielding, according to a typical course of a yielding curve, it is sufficient to introduce halved doses of nitrogen in relation to the ones used in the experiment. The data in Table 1 evidently point to the fact that yields of lettuce and radish cultivated in the spring were higher than those originating from the autumn.

Table 1

Lettuce and radish yield

Form of nitrogen	Nitrogen dose [g N · pot^{-1}]	Spring harvest		Autumn harvest	
		Lettuce	Radish	Lettuce	Radish
		[g d.m. · pot^{-1}]			
	0.0	10.1	6.8	1.0	2.3
$(NH_4)_2SO_4$	0.5	12.8	7.4	2.8	3.6
	1.0	14.9	8.9	3.9	4.2
	1.5	19.9	9.9	4.9	5.4
	2.0	7.6	3.4	1.7	1.7
	3.0	4.6	2.8	1.0	1.2
Mean value		12.0	6.5	2.9	3.2
$Ca(NO_3)_2$	0.5	15.2	8.1	3.3	3.1
	1.0	18.5	9.4	5.5	4.9
	1.5	23.4	10.2	6.9	5.9
	2.0	12.6	5.5	3.0	2.5
	3.0	9.8	2.4	1.6	1.0
Mean value		15.9	7.1	4.1	3.5
NH_4NO_3	0.5	13.6	7.3	3.9	4.1
	1.0	16.2	8.8	4.3	5.4
	1.5	21.9	11.4	7.8	7.3
	2.0	13.1	3.8	4.1	4.2
	3.0	9.1	2.0	2.4	3.5
Mean value		14.8	6.7	4.5	4.9
$CO(NH_2)_2$	0.5	13.9	7.5	3.9	3.4
	1.0	15.2	8.4	5.0	4.8
	1.5	18.9	9.4	7.1	6.2
	2.0	11.8	2.9	3.7	3.6
	3.0	7.9	1.2	1.4	1.9
Mean value		13.5	5.9	4.2	4.0
$LSD_{0.05}$		1.43	0.88	0.76	0.29

Taking into account the form of nitrogen present in fertilizers, average the highest lettuce yields were obtained when plants were fertilized with calcium and ammonium saltpetre, while the lowest ones resulted from fertilization with this element in the form of ammonium sulfate. The yields of lettuce fertilized with urea were of a medium size. Similar results were reported by [13], who used 5.5 g of nitrogen in the form of ammonium saltpetre, which caused an increase in lettuce yield size in comparison with control treatment. The same authors proved that increased dose of nitrogen fertilizer brought about considerably smaller yield size.

The data present in Table 1 apparently prove that in the case of radish as well as of lettuce higher yields were also obtained in the spring. Considering average amounts of particular treatments it should be stated that generally, in the autumn the yields were nearly twice lower. This can be confirmed by the other authors [11], who, in their research on the effect of cultivation term on nitrates(V) content in radish roots, reported higher leaves mass from the spring cultivation and slightly lower – from the autumn cultivation. According to Kobryn [10] an important role is also played by the term of plants sowing. Earlier radish sowing did effect on obtaining higher yields of radish roots.

Noticeable influence on yield size had nitrogen dose. Initially, as the mentioned dose increased there was recorded significant increase in roots yield, but when the dose exceeded 1.5 g $\cdot$ pot^{-1} yield size did considerably diminish. It should be stated that there was no evidence of a significant effect of any nitrogen form on radish yield size, as average yields of roots from each experimental treatment were of similar values. The only exception was cultivation of this plant in the autumn, since there were recorded some tendencies of root yield to increase when ammonium saltpetre and urea were used as fertilizers.

Nitrogen fertilization did markedly effect on $N\text{-}NO_3$ content in cultivated plants. Nitrates(V) concentration in both plant species cultivated in the autumn was lower than the one featuring these vegetables cultivated in the spring, which confirms the conclusions by other authors. Buniak [14] reported that regardless the plants species definitely more nitrates(V) were present in them in the spring than in the summer, while Lis [9] reported that early cultivars of potato accumulate higher amounts of nitrates(V) than later cultivars. However, there do exist literature records with other results. Michalik and Szwonek [7] after Hermanowicz reported that in the experiment with spinach the mentioned author proved higher nitrates(V) content in plants cultivated in the autumn. Also Bram et al [15] obtained lower nitrates(V) content in lettuce cultivated in summer season in comparison with nitrates(V) content in plants cultivated in the autumn. In our research nitrates(V) content could be, to high extend, modified by photoperiod conditions in the course of plant vegetation.

The data shown in Figs. 1–4 apparently prove that nitrate(V) form of nitrogen in both species of cultivated plants increased as nitrogen fertilizer dose increased, regardless particular forms of nitrogen present in fertilizer applied.

Lettuce cultivated in the spring contained higher quantity of $N\text{-}NO_3$ than in autumn season (Figs. 1–2). Yet the most significant influence on nitrates(V) accumulation by this vegetable, regardless its cultivation term, had nitrogen dose and the form this component was used. In both terms of lettuce cultivation the lowest amount of $N\text{-}NO_3$ in this plant was recorded for its fertilization with ammonium sulfate, while the highest quantities of nitrogen occurred after fertilization with ammonium and calcium saltpetre. Fertilization with urea caused nitrates(V) accumulation ranging average values, yet in this case attention should be paid to much higher content of mineral nitrogen in lettuce

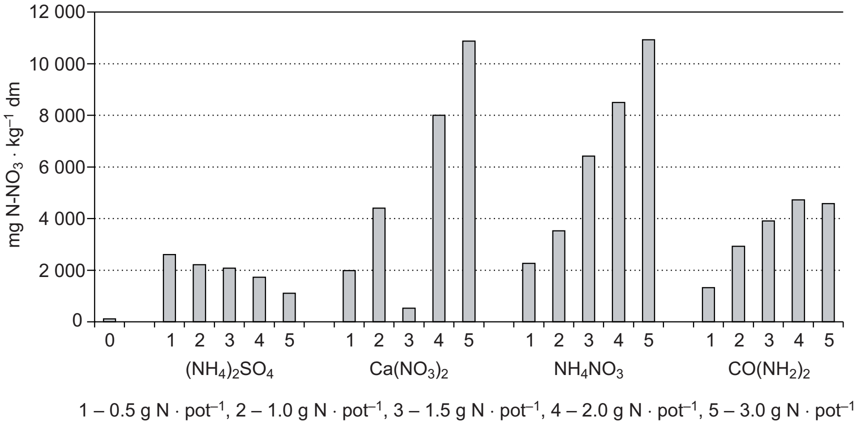

Fig. 1. $N\text{-}NO_3$ content in spring-cultivated lettuce

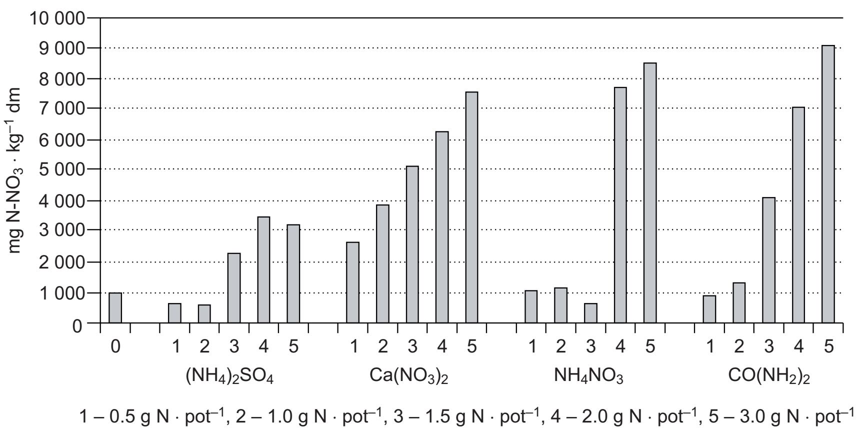

Fig. 2. $N\text{-}NO_3$ content in autumn-cultivated lettuce

fertilized with urea in the autumn than in the spring. The latter phenomenon was probably observed due to slow release of nitrogen as a result of the process of fertilizer hydrolysis.

Apart from the above results, in spring-cultivated lettuce there was observed relatively proportional increase in $N\text{-}NO_3$ according to increasing amount of nitrogen in soil, while in the same plant cultivated in later term significant increase in this form of nitrogen was noticeable only at nitrogen doses ranging 2 and 3 g N $\cdot$ pot^{-1}. These rather low contents of $N\text{-}NO_3$ in lettuce, observed especially for plants fertilization with nitrogen in the amount of 1.5 g N $\cdot$ pot^{-1}, could result from dilution of this component as generally in our investigation at that dose there were recorded the highest plant yields.

Similar results were obtained in the experiments by Kalembasa and Deska [13], who proved that gradually increasing doses of ammonium saltpetre brought about considerable increase in nitrates(V) amount in lettuce leaves. Also in research by Zalewski [16], lettuce fertilized with higher nitrogen doses accumulated higher quantities of nitrates(V). Michalik [17, 18] on the basis of pot experiment, stated that nitrates(V) content in lettuce increased according to increasing doses of nitrogen in earlier terms of cultivation. According to Barczak and Cwojdzinski [19] the increase in nitrogen dose causes increased uptake of this element by plants and, therefore its usability for protein synthesis is weaker, which results in highest contribution of nitrate(V) fraction in total the nitrate. As it was reported by Rogozinska et al [20] nitrates(V) content in mature potato tubers increased proportionally to increased doses of mineral nitrogen fertilizers.

The results shown in Figs. 3 and 4 confirm previous observations that higher amounts of nitrates(V) were accumulated in radish roots in the autumn, and concentration of this form increased with nitrogen dose. The highest increase in $N\text{-}NO_3$ content in radish roots in comparison with the amount of this nitrogen form assayed in cultivated

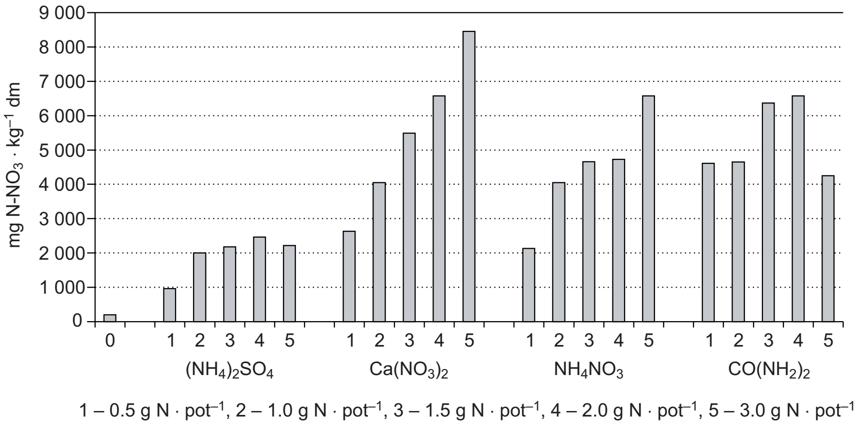

Fig. 3. $N\text{-}NO_3$ content in radish roots cultivated in the spring

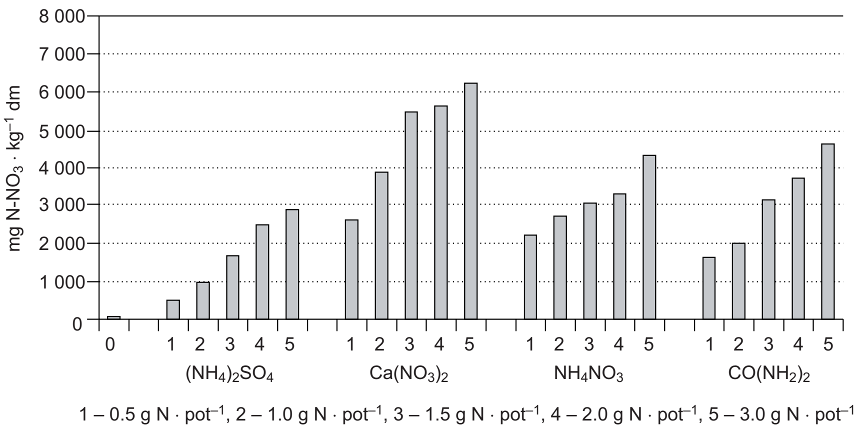

Fig. 4. $N\text{-}NO_3$ content in radish roots cultivated in the autumn

plants originating from control treatment was observed after application of ammonium and calcium sulfate, while the lowest one occurred after plant fertilization with ammonium sulfate. As far as this vegetable is concerned, it should be stressed that significant influence of amide form of nitrogen on the increase in nitrates(V) accumulation takes place regardless its cultivation term. The results obtained in our research were, in most cases, in agreement with those found in the literature, among others by Jagiello et al [21] who reported that nitrates(V) content in beet and carrot roots depended on fertilizer dose and kind and it increased as the amount of added fertilizer increased. Czekala [22] proved the effect of fodder beet cultivar on nitrates(V) accumulation in its roots and leaves. Michalik [17, 18] found that the form of nitrogen introduced effected on nitrates(V) content in vegetables and that fertilizers featuring slow release of nitrogen caused the increase in plant nitrates(V) content to a lower degree. Lettuce fertilized with ammonium nitrate(V) characterized higher nitrates(V) content as compared with lettuce fertilized with urea. Similarly, Goralski and Kaminska-Dudek [23], comparing the effect of ammonium saltpetre and urea, reported that ammonium nitrate(V) content in plant material was always higher after application of ammonium saltpetre than after urea fertilization. Jurgiel-Malecka and Suchorska--Orlowska [24] stated that the kind of fertilizer applied (urea, ammonium saltpetre, calcium saltpetre) did not significantly effect on nitrate(V) content in leaves of bulb plants subjected to examination. Kalembasa and Deska [13] comparing the effect of nitrogen used in vermicompost, manure and mineral fertilizers on yield, total nitrogen content and nitrates(V) content in lettuce leaves, reported that increased doses of ammonium saltpetre did considerably increase nitrates(V) content, while in the case of vermicompost $N\text{-}NO_3$ concentration showed only slight increase. Similar results were obtained in our investigation – the lowest nitrates(V) content was recorded in plants cultivated on the treatments where ammonium sulfate was applied. According to Michalik and Borkowski [6] physiologically acid character of ammonium sulfate could markedly lower medium pH which in turn could influence on the increase in nitrates(V) content.

In the conditions of investigation conducted, regardless cultivation term, higher amounts of nitrates(V) were accumulated by lettuce than by radish. Considering total nitrogen and mineral nitrogen content in soil, it was reported that as nitrogen dose increased its content in surface soil layer also increased and this amount was dependent on the kind of nitrogen fertilizer used and on cultivated plant species. Higher quantities of mineral nitrogen contained soils fertilized with ammonium saltpetre, calcium saltpetre and ammonium sulfate, than soil fertilized with urea. N-mineral content in soil after lettuce and radish cultivation on particular combinations was similar. Total nitrogen content in soil was related to cultivated plant species. The highest quantity of this component was detected in soils after radish cultivation.

$N\text{-}NO_3$ contribution to mineral nitrogen depended on the form of fertilizer applied. The highest amounts of this nitrogen form was determined in soils fertilized with calcium and ammonium saltpetre, as well as with urea, while the lowest one – after the use of ammonium sulfate (Figs. 5, 6). After cultivation of plants fertilized with calcium

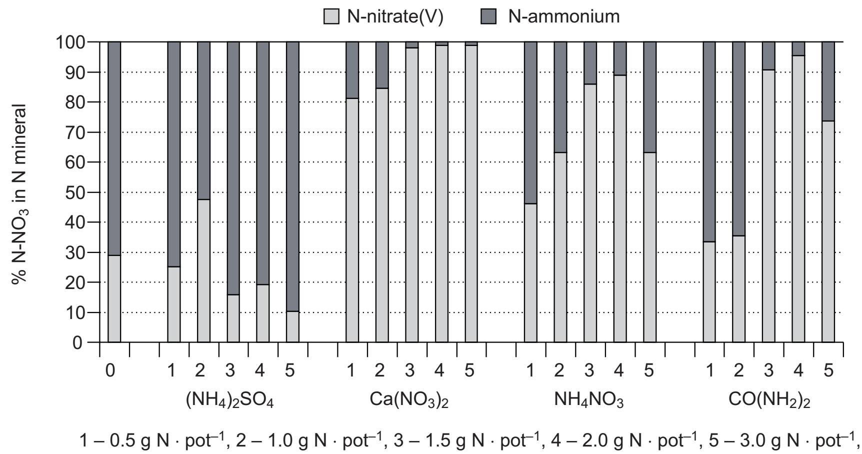

Fig. 5. Percentage contribution of $N\text{-}NO_3$ in mineral N in soil after lettuce cultivation

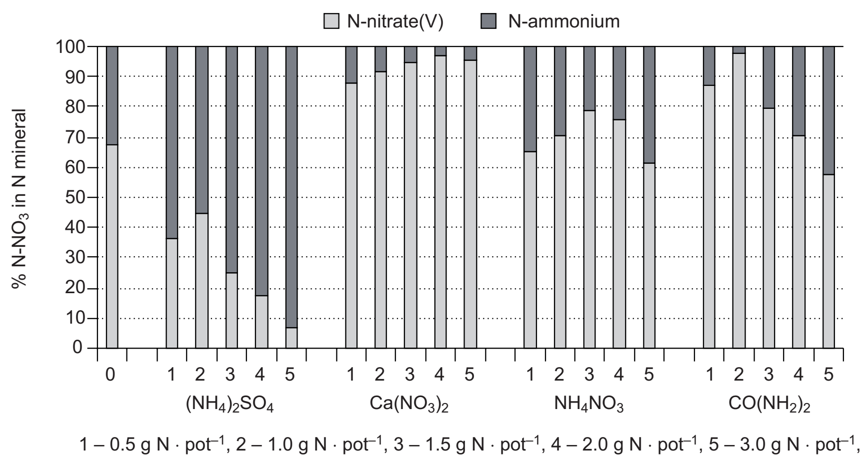

Fig. 6. Percentage contribution of $N\text{-}NO_3$ in mineral N in soil after radish cultivation

saltpetre the contribution of soil $N\text{-}NO_3$ in mineral nitrogen content was high and it ranged, depending on particular species cultivated, from 75 to 94 %.

The use of ammonium saltpetre had caused decrease in content of $N\text{-}NO_3$ accumulation in soil. In soils, where calcium saltpetre was applied, after completing the experiment was 50 to 70 % more of $N\text{-}NO_3$ depending on cultivated plant. Similar quantities of this nitrogen form were found in soils fertilized with urea. The use of ammonium saltpetre was also decisive regarding $N\text{-}NO_3$ accumulation in soil, although these amounts were considerably lower, in comparison with calcium saltpetre and not exceeding the range of about 50 to 70 %, according to plant species cultivated. Similar quantities of this nitrogen form were found in soils fertilized with urea.

The lowest amount of $N\text{-}NO_3$ in relation to the dose of mineral nitrogen after plant harvesting were determined in soils fertilized with ammonium sulfate. These values ranged from 10 to 30 % and nitrate(V) nitrogen was the remaining part. In all the cases discussed the contents of nitrate(V) nitrogen were dependent on fertilizer dose and they were the higher the higher dose was applied. According to Ciecko et al [25] nitrogen fertilization caused higher concentration of ammonium and nitrate(V) nitrogen in soil solution. The authors, on the basis of long-term experiments, proved that under the influence of high-dose nitrogen fertilization there occurred a tendency in soils to increase contribution of nitrate(V) nitrogen in mineral nitrogen.

Conclusions

1. Out of two vegetable species subjected to examination lettuce accumulated higher amounts of nitrate(V) nitrogen than radish. In both of plants the highest contents of $N\text{-}NO_3$ was determined after application of highest doses of this element.

2. Higher contents of nitrates(V) in the lettuce leaves and radish roots were determined when cultivation took place in the spring. In the autumn nitrates(V) contents showed decreased values.

3. Regardless plant species, the highest amount of nitrates(V) were accumulated by plants fertilized with calcium and ammonium saltpetre, while the lowest ones belonged to vegetable fertilized with ammonium sulfate.

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WPŁYW DAWKI I FORMY AZOTU NA ZAWARTOŚĆ AZOTANÓW(V) W WYBRANYCH GATUNKACH WARZYW

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Abstrakt: Celem prezentowanej pracy była ocena wpływu stosowania wzrastających dawek różnych form azotu na gromadzenie się azotanów(V) w sałacie i korzeniach rzodkiewki. Badania realizowano poprzez ścisłe doświadczenia wegetacyjne, które prowadzono w latach 2003–2005 w hali wegetacyjnej. W każdym roku badań wiosną i w okresie jesiennym oba gatunki roślin nawożono azotem w ilości; 0,5; 1,0; 1,5; 2,0; i 3,0 g N · wazon^{-1}, stosując go w postaci $(NH_4)_2SO_4$, $Ca(NO_3)_2$, NH_4NO_3 oraz $CO(NH_2)$. Doświadczenie założono na glebie lekkiej o odczynie słabo kwaśnym, niskiej zawartości potasu, średniej fosforu oraz wysokiej magnezu. Wpływ dawki i formy azotu oceniono analizując masę plonów uprawianych roślin, zawartość azotu ogólnego oraz azotu azotanowego(V). W glebach po zakończeniu badań określono zawartość azotu mineralnego. Wykazano, że plony zarówno sałaty, jak i rzodkiewki wzrastały w miarę zwiększania dawki azotu do 1,5 g N · wazon^{-1}. Najbardziej plonotwórczo w przypadku sałaty działała saletra wapniowa, natomiast w przypadku rzodkiewki saletra amonowa. Znacznie większe plony obu roślin z tych samych obiektów zebrano, uprawiając je w okresie wiosennym. Najwyższą koncentrację azotu azotanowego(V) oznaczono w obu roślinach wówczas, gdy nawożono je najwyższą dawką azotu, jednak zawsze większe zawartości tej formy azotu stwierdzano w sałacie niż rzodkiewce. Mniej azotanów(V) w każdym z badanych gatunków oznaczono wiosną niż jesienią. Niezależnie od gatunku, najwięcej azotanów(V) gromadziły rośliny nawożone saletrą wapniową i amonową, a najmniej, gdy w ich uprawie stosowano siarczan amonu.

Słowa kluczowe: nawożenie azotem, formy azotu, azot azotanowy(V), termin uprawy, sałata, rzodkiewka

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EFFECT OF PHOSPHORUS AND POTASSIUM FERTILIZATION ON NITRATES(V) CONTENT IN MAIZE AND BUCKWHEAT

WPŁYW NAWOŻENIA FOSFOREM I POTASEM NA ZAWARTOŚĆ AZOTANÓW W KUKURYDZY I GRYCE

Abstract: Investigation was carried out in the conditions of cold greenhouse in a two-year-cycle and even doses of nitrogen introduced into soil in different chemical forms provided a background for application of increasing doses of phosphorus and potassium amounting 0.5; 1.0 and 1.5 g P and K · pot^{-1}. The effect of these components was assessed by determination of yield mass of experimental plants (maize and buckwheat) as well as accumulation of nitrate(V) nitrogen in aboveground plant parts. Regarding the conditions of our investigation, increasing doses of phosphorus decided neither about maize nor buckwheat yielding, while potassium added to soil, which was at the same time provided with even doses of nitrogen, on treatments fertilized with urea did significantly decrease maize yield mass. Application of different nitrogen fertilizers, at simultaneous increase in phosphorus amount in soil, resulted in diversified nitrate(V) contents in maize and buckwheat. Phosphorus diminished $N\text{-}NO_3$ content in maize fertilized with ammonium saltpetre and urea. In the case of buckwheat this effect was observed only when this plant was fertilized with urea. On the remaining objects increasing doses of phosphorus did not modify the content of this nitrogen form in experimental plants. The use of potassium did evidently decrease nitrate(V) content in buckwheat fertilized with all kinds of nitrogen fertilizers except for ammonium sulfate. As far as maize was concerned, experiments proved that the decrease in nitrate(V) concentration as a result of higher doses of potassium fertilization occurred only when nitrogen was applied in the form of ammonium saltpetre. In plants cultivated on the remaining experimental treatments $N\text{-}NO_3$ concentration reached similar values. A dominant form of mineral nitrogen was nitrate(V) nitrogen.

Keywords: nitrogen, nitrogen fertilizers, phosphorus fertilization, potassium fertilization, $N\text{-}NO_3$ maize, buckwheat

In a number of scientific elaborations their authors stress that soil richness in nutrients can be a decisive factor regarding nitrogen absorption by plants, as well as accumulation of nitrate(V) form of this chemical element. Potassium and phosphorus play an important role in this process. Czuba [1] reported that plants cultivated in the

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conditions of poor supply with phosphorus accumulate nitrate(V) in older tissues, while those abundantly provided with nitrogen, at simultaneous potassium deficiency, feature the ability to accumulate in their tissues amines and ammonium ions. Similar results obtained Cieslik [2] who related that in different plant species fertilization with high doses of nitrogen, at phosphorus deficiency in soil, resulted in increased amount of nitrate(V) in plants. In experiments by Nowacki [3] as well as by Munzert and Lepschy [4] there was observed decreased nitrate(V) content under the influence of higher phosphorus doses, although in potatoes this relation was not observed. Also numerous authors reported that increased potassium fertilization, at continuous supply of nitrogen, did decrease nitrate(V) content in the examined plants [5, 6]. Yet different conclusions were drawn by Ciecko et al [7] who proved that increasing doses of potassium, at continuous nitrogen fertilization, were of no importance for nitrate(V) content in potato tubers. The aim of this investigation was the assessment of the effect application of increasing doses of phosphorus and potassium, at even doses of nitrogen fertilization but with different nitrogen compounds, exerted on nitrate(V) accumulation in maize and buckwheat.

Material and methods

Research was conducted on the basis of exact cultivation – pot experiments involving application of increasing doses of phosphorus and potassium ranging 0.5; 1.0 and 1.5 g · pot^{-1}, at even level of nitrogen fertilization using different chemical forms of nitrogen (ammonium salptetre, calcium saltpetre, urea and ammonium sulfate). The choice of nitrogen dose was based on the results of previous experiments so that plants were provided with the conditions for optimum yielding and, at the same time, for increased accumulation of nitrate(V) in their aboveground parts. As far as maize cultivation was concerned, this dose amounted 1.5 g N · pot^{-1}, while in the case of buckwheat it equaled 1.0 g N · pot^{-1}. Investigation was carried out on light soil of acid reaction, medium – rich in plant – accessible phosphorus. The content of absorbable phosphorus was low, while magnesium content was of a high value. The experiment was conducted within two-year period in Wagner pots of 5 kg volume, in four replications.

In the course of plant growing period there took place detailed observations regarding plants growth and development and, if needed, there was applied chemical control of diseases and pests. After the harvest of experimental plants there were determined their yields, as well as harvested plants were subjected to analysis involving the contents of total nitrogen and nitrate(V) nitrogen. The results obtained were expressed as mean values for the whole examination period. The data were processed according to statistical analysis using analysis of variance due to Tukey's test at level of significance 0.05.

Results and discussion

The results shown in Table 1 point to the fact that average maize yields were of similar size, regardless the kind of nitrogen fertilizer applied. The only exceptions were experimental treatments fertilized with calcium saltpetre, where maize yields were considerably lower. In the case of buckwheat cultivation significantly lower yield was obtained for plants fertilized with ammonium sulfate, while the highest one when ammonium saltpetre was used. For the remaining fertilizers, although they did not modify yield size to a high degree, the differences between particular treatments occurred to be statistically proved.

Table 1

Experimental plants yields

Form of nitrogen	Phosphors dose g P · pot^{-1}	Maize	Buckwheat	Potassium dose g K · pot^{-1}	Maize	Buckwheat
		g dm · pot^{-1}			g dm · pot^{-1}	
$(NH_4)_2SO_4$	0.0	70.4	21.9	0.0	78.2	20.6
	0.5	71.6	22.3	0.5	79.6	21.3
	1.0	74.5	21.4	1.0	76.8	19.6
	1.5	74.7	19.0	1.5	78.3	19.8
Mean value		73.6	20.9	Mean value	78.2	20.3
$Ca(NO_3)_2$	0.0	66.2	24.4	0.0	72.2	27.6
	0.5	66.8	25.1	0.5	73.6	28.1
	1.0	67.3	24.8	1.0	70.4	27.7
	1.5	67.1	26.6	1.5	74.0	27.3
Mean value		67.0	25.5	Mean value	72.6	27.7
NH_4NO_3	0.0	72.9	26.0	0.0	76.5	26.3
	0.5	73.1	26.7	0.5	77.4	26.8
	1.0	71.5	25.8	1.0	75.5	28.9
	1.5	68.1	27.3	1.5	77.6	27.8
Mean value		70.9	26.6	Mean value	76.8	27.5
$CO(NH_2)_2$	0.0	70.4	23.6	0.0	78.0	25.4
	0.5	72.0	23.9	0.5	79.3	26.2
	1.0	73.3	24.3	1.0	71.6	25.3
	1.5	71.5	24.2	1.5	71.3	25.1
Mean value		72.2	24.1	Mean value	75.1	25.5
LSD						
I for nitrogen form		1.04	0.73		1.08	1.62
II for phosphorus/potassium dose		0.96	0.65		0.90	2.29
III for interaction I/II		2.14	1.48		2.01	5.13

* dm = dry matter.

The introduction of increasing doses of phosphorus, at even nitrogen fertilization, did not effect on maize yielding, yet on the treatments fertilized with ammonium sulfate, especially at higher P doses, there was observed a tendency to obtain increased yield size values (Table 1). The mentioned relation was not recorded on treatments where buckwheat was cultivated using high P dose.

In the experiment involving increasing doses of potassium, at even level of nitrogen fertilization both maize and buckwheat yields were diversified and they did significantly depend on the kind of nitrogen fertilizer used (Table 1). The highest maize yields were obtained when plants were fertilized with ammonium sulfate and ammonium saltpetre, while the lowest ones when calcium saltpetre was applied. Buckwheat occurred to react differently to diverse nitrogen forms. The lowest amounts of buckwheat dry matter were harvested from treatments fertilized with ammonium sulfate, while the remaining fertilizers, especially both saltpetres, resulted in significantly higher yields.

Introduction of increasing potassium doses into soil fertilized with even doses of different nitrogen forms did not undoubtedly influence the yielding of experimental plants, except for the treatment with urea-fertilized maize. Results obtained in our investigation can be confirmed by the literature data. Gasior and Kaniuczak [8] reported that the increase in mineral fertilizer dose brought about increased yields and the mentioned increase was higher on treatments fertilized with NPK in comparison with those fertilized only with PK.

Nitrate(V) content, both in maize and in buckwheat depended on the form of nitrogen applied. The highest amounts of N-NO_3 were determined in plants fertilized with calcium and ammonium saltpetre, while the lowest quantities – when ammonium sulfate was used. Maize and buckwheat fertilized with urea contained average amounts of this nitrogen form.

Application of increasing dose of phosphorus, at simultaneous fertilization with different nitrogen fertilizers, did diversify the amount of nitrate(V) nitrogen in maize and in buckwheat (Figs. 1, 2). The highest contents of N-NO_3 in both plants was found after the use of calcium and ammonium saltpetre, while the lowest amounts of nitrate(V) nitrogen were recorded after fertilization with ammonium sulfate. Average

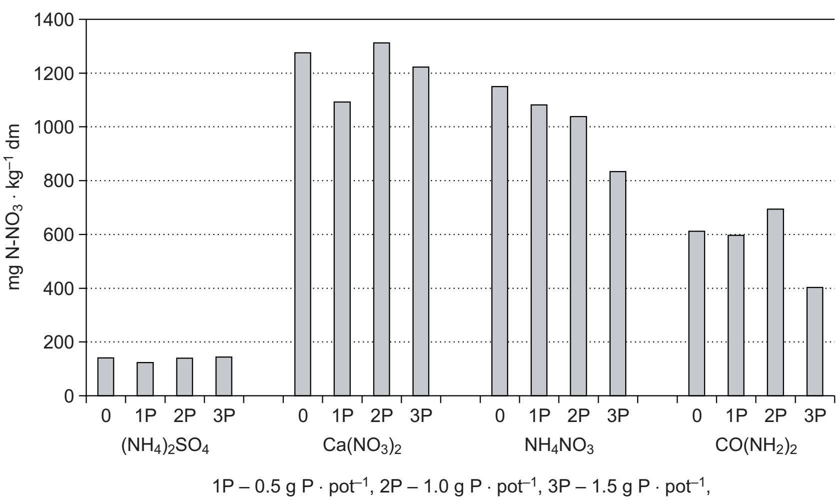

Fig. 1. Nitrate(V) content in maize fertilized with phosphorus at fertilization with different nitrogen forms

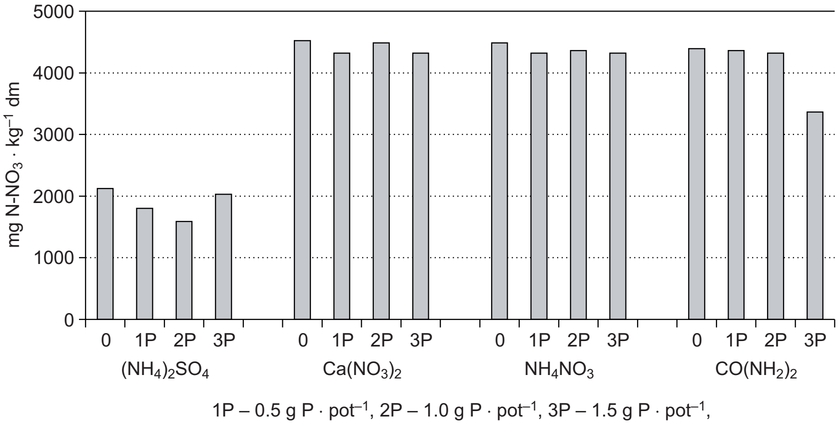

Fig. 2. Nitrate(V) content in buckwheat fertilized with phosphorus at fertilization with different nitrogen forms

amounts of nitrate(V) were determined in plants treated with urea. In maize, differences in this component content, depending on the form of nitrogen applied, were considerable (in some cases 10 times higher values) while in buckwheat they were not so profound.

Better supply in phosphorus decreased $N\text{-}NO_3$ concentration in maize fertilized with ammonium saltpetre and urea. In buckwheat, this phenomenon was observed only when the plant was fertilized with urea (Figs. 1, 2). Increasing dose of phosphorus on the remaining treatments was of no effect regarding the content of this form of nitrogen in experimental plants. Nowacki [3] reported after Sharer and Siebel, that phosphorus resulted in the decrease of nitrate(V) content, but only at low and medium nitrogen doses, while in the conditions of high-dose-nitrogen fertilization protective activity of phosphorus disappeared. Czuba [1] stated that even older plants cultivated in the conditions of deficient phosphorus supply plants could accumulate excessive amounts of nitrate(V) in their tissues. Gasior and Kaniuczak [8] recorded that nitrate(V) content in hay was much higher after the use of full fertilization with NPK than with P and K solely.

Application of increased potassium doses did explicitly decreases nitrate(V) content in buckwheat fertilized the examined nitrogen fertilizers, except for ammonium sulfate. According to the literature data [9] in the conditions of nitrogen fertilization the response of grass species to increased amounts of potassium was expressed by the possibility of nitrate(V) reduction. In the case of maize it was possible to prove that the decrease in nitrate(V) concentration as a result of increased potassium fertilization took place only when nitrogen was introduced in the form of ammonium saltpetre (Fig. 3). In plants cultivated on the remaining treatments $N\text{-}NO_3$ contents reached similar level. Ciecko et al [7] proved that in their experiments potassium deficiency caused nitrate(V) accumulation, as well as accumulation of organic nitrogen in plants in the form of amino acids and amides.

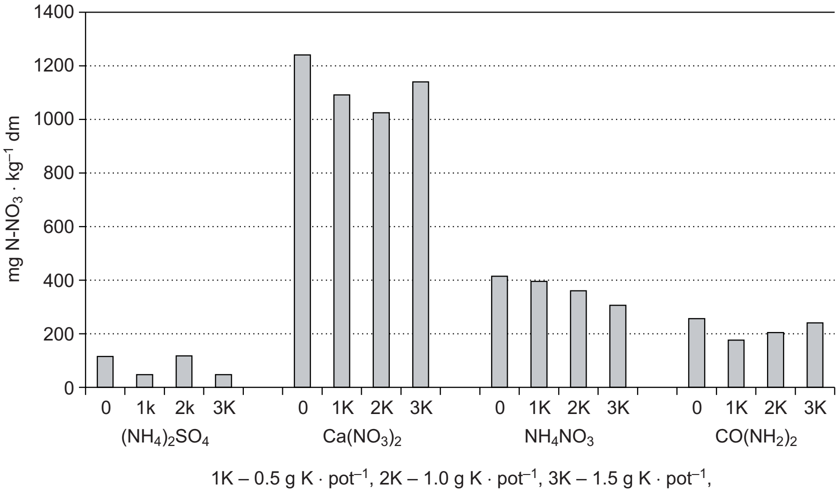

Fig. 3. Nitrate(V) content in maize fertilized with potassium at fertilization with different nitrogen forms

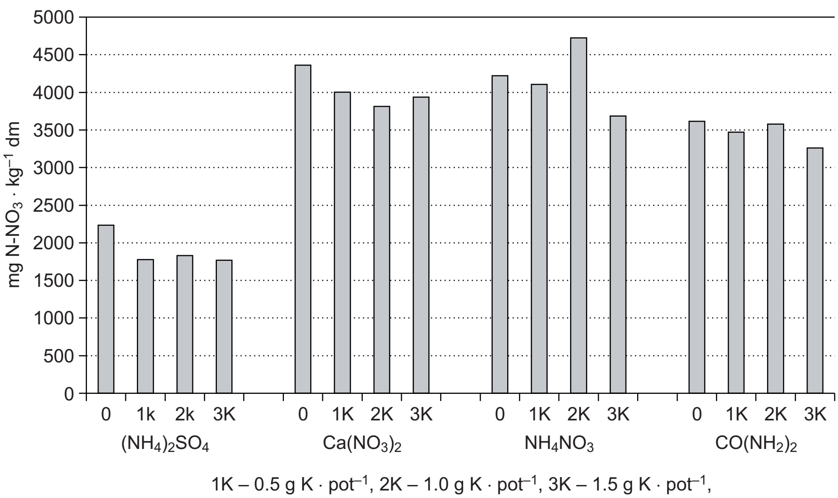

Fig. 4. Nitrate(V) content in buckwheat fertilized with potassium at fertilization with different nitrogen forms

After investigation had been finished, there was also estimated mineral nitrogen concentration in soil. In Figures 5 and 6 there was shown nitrate(V) nitrogen contribution to total amount of mineral nitrogen. The highest quantities of $N\text{-}NO_3$ were determined in soils collected from treatments fertilized with ammonium and calcium saltpetre and its contribution to mineral nitrogen on these treatments ranged 80 %. The contribution of this nitrogen form did apparently decrease according to the increase in phosphorus dose on each of the examined treatments (Fig. 5).

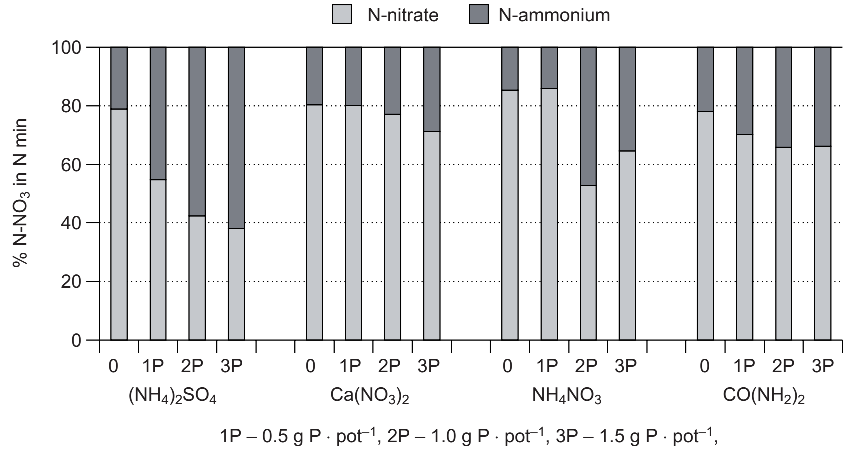

Fig. 5. $N\text{-}NO_3$ contribution to mineral nitrogen in soil fertilized with phosphorus at fertilization with different nitrogen forms

Application of increasing potassium doses at even – dose nitrogen fertilization was decisive as far as percentage contribution of nitrate(V) nitrogen in mineral nitrogen was concerned (Fig. 6).

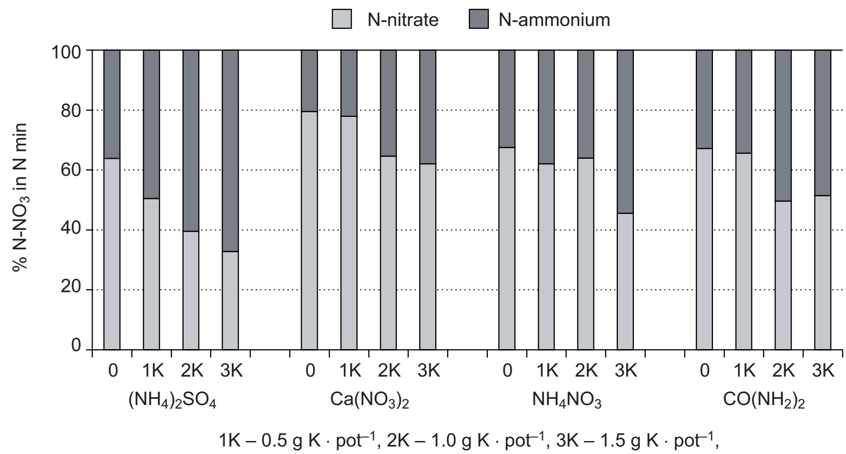

Fig. 6. $N\text{-}NO_3$ contribution in mineral nitrogen in soil fertilized with potassium at fertilization with different nitrogen forms

The highest amount of $N\text{-}NO_3$ was determined in soils fertilized with calcium saltpetre where contribution of this nitrogen form in mineral nitrogen ranged average 70 %, while the lowest quantities were assayed on treatments fertilized with ammonium sulfate. On these treatments there were determined average 40 % contributions of $N\text{-}NO_3$ to mineral nitrogen. On all experimental treatments there was recorded decreased contribution of nitrate(V) nitrogen to total scope of mineral nitrogen as potassium dose increased.

Conclusions

1. Introduction of phosphorus and potassium to soil fertilized with even dose of different nitrogen forms did not significantly influence on maize and buckwheat yield.

2. Increasing doses of phosphorus at nitrogen fertilization diversified nitrate(V) content in maize on treatments fertilized with ammonium saltpetre and urea while in the case of buckwheat only on treatments when urea fertilizer was used. On these treatments, according to the increase in phosphorus dose concentration of the $N\text{-}NO_3$ form decreased.

3. Potassium fertilization decreased nitrate(V) nitrogen content only on treatments fertilized with ammonium salpeter. On the remaining combinations no effect of this component was recorded regarding nitrate(V).

4. After experiment had been finished, a dominant form of mineral nitrogen was nitrate(V) nitrogen in soils of all treatments.

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Abstrakt: Badania prowadzono w warunkach hali wegetacyjnej w cyklu dwuletnim, na tle jednakowych dawek azotu wprowadzanego do gleby w różnych formach chemicznych stosowano wzrastające dawki fosforu i potasu w ilościach 0.5; 1.0 i 1.5 g P i K $\cdot$ wazon^{-1}. Działanie tych składników oceniano, określając masę plonów roślin doświadczalnych (kukurydzy i gryki) oraz nagromadzenie azotu azotanowego(V) w ich częściach nadziemnych. W warunkach prowadzonych badań wzrastające ilości fosforu nie decydowały o plonowaniu kukurydzy i gryki, natomiast potas dodawany do gleby na tle jednakowego nawożenia azotem na obiektach nawożonych mocznikiem znacznie zmniejszał masę plonów kukurydzy. Stosowanie nawozów azotowych w różnych formach, przy jednocześnie wzrastającej ilości fosforu w podłożu, różnicowało zawartość azotanów(V) w kukurydzy i gryce. Fosfor obniżał zawartość $N\text{-}NO_3$ w kukurydzy nawożonej saletrą amonową i mocznikiem, natomiast w gryce tylko wówczas, gdy nawożona była mocznikiem. Na pozostałych obiektach wzrastające dawki fosforu nie modyfikowały zawartości tej formy azotu w roślinach doświadczalnych. Stosowanie potasu wyraźnie zmniejszało zawartość azotanów(V) w gryce nawożonej wszystkimi nawozami azotowymi z wyjątkiem siarczanu amonu. W przypadku kukurydzy wykazano, że obniżenie koncentracji azotanów(V) w wyniku zwiększenia nawożenia potasem miało miejsce jedynie wówczas, gdy azot stosowano w postaci saletry amonowej. W roślinach uprawianych na pozostałych obiektach badawczych koncentracja $N\text{-}NO_3$ kształtowała się na zbliżonym poziomie. W glebach po zakończeniu doświadczenia dominującą formą azotu mineralnego był azot azotanowy(V).

Słowa kluczowe: azot, nawozy azotowe, nawożenie fosforem, nawożenie potasem, zawartość $N\text{-}NO_3$, kukurydza, gryka

Varia

Invitation for ECOpole '10 Conference

CHEMICAL SUBSTANCES IN ENVIRONMENT

We have the honour to invite you to take part in the 19th annual Central European Conference ECOpole '10, which will be held in **13–16 X 2010** (Thursday–Saturday) on Wilhelms Hill at Uroczysko in Piechowice, the Sudety Mts., Lower Silesia, PL.

The Conference Programme includes oral presentations and posters and will be divided into five sections:

The Conference Programme includes oral presentations and posters and will be divided into five sections – SI–SV:
- SI Chemical Pollution of Natural Environment and its Monitoring
- SII Environment Friendly Production and Use of Energy
- SIII Risk, Crisis and Security Management
- SIV Forum of Young Scientists and Environmental Education in Chemistry
- SV Impact of Environment Pollution on Food and Human Health

The Conference language is English.

Contributions to the Conference will be published as:
- abstracts on the CD-ROM (0.5 page of A4 paper sheet format)
- extended Abstracts (4–6 pages) in the semi-annual journal *Proceedings of ECOpole*
- full papers will be published in successive issues of the *Ecological Chemistry and Engineering/Chemia i Inżynieria Ekologiczna* (Ecol. Chem. Eng.) ser. A or S.

Additional information one could find on the Conference website:

ecopole.uni.opole.pl

The deadline for sending the Abstracts is **15.07.2010** and for the Extended Abstracts: **1.10.2010**. The actualised list (and the Abstracts) of the Conference contributions accepted for presentation by the Scientific Board, one can find (starting from 15.07.2010) on the Conference website.

The papers must be prepared according to the Guide for Authors on Submission of Manuscripts to the Journals.

The Conference fee is 300 € (covering hotel, meals and transportation during the Conference). It could be reduced (to 170 €) for young people actively participating in the Forum of Young Scientists. But the colleague has to deliver earlier the Extended

Abstract (4–6 pages) of his/her contribution (deadline is on **15.08.2010**), and a recommendation of his/her Professor.

At the Reception Desk each participant will obtain a CD-ROM with abstracts of the Conference contributions as well as Conference Programme (the Programme will be also published on this site).

Further information is available from:
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Zapraszamy
do udziału w Środkowoeuropejskiej Konferencji
ECOpole '10
w dniach 13–16 X 2010

SUBSTANCJE CHEMICZNE W ŚRODOWISKU PRZYRODNICZYM

Będzie to dziewiętnasta z rzędu konferencja poświęcona badaniom podstawowym oraz działaniom praktycznym dotycząca różnych aspektów ochrony środowiska przyrodniczego. Odbędzie się ona w ośrodku „Uroczysko" na Wzgórzu Wilhelma w Piechowicach, koło Szklarskiej Poręby. Doroczne konferencje ECOpole mają charakter międzynarodowy i za takie są uznane przez Ministerstwo Nauki i Szkolnictwa Wyższego.

Obrady konferencji ECOpole '10 będą zgrupowane w pięciu sekcjach:

– SI Chemiczne substancje w środowisku przyrodniczym oraz ich monitoring
– SII Odnawialne źródła energii i jej oszczędne pozyskiwanie oraz użytkowanie
– SIII Zarządzanie środowiskiem w warunkach kryzysowych
– SIV Forum Młodych (FM) i Edukacja prośrodowiskowa
– SV Wpływ zanieczyszczeń środowiska oraz żywności na zdrowie ludzi.

Materiały konferencyjne będą opublikowane w postaci:

– abstraktów (0,5 strony formatu A4) na CD-ROM-ie;
– rozszerzonych streszczeń o objętości 4-6 stron w półroczniku *Proceedings of ECOpole*;
– artykułów: w abstraktowanych czasopismach: *Ecological Chemistry and Engineering/Chemia i Inżynieria Ekologiczna* (*Ecol. Chem. Eng.*) ser. A i S oraz niektórych w półroczniku *Chemia – Dydaktyka – Ekologia – Metrologia*.

Termin nadsyłania angielskiego i polskiego streszczenia o objętości 0,5–1,0 strony (wersja cyfrowa + wydruk) planowanych wystąpień upływa w dniu 15 lipca 2010 r. Lista prac zakwalifikowanych przez Radę Naukową Konferencji do prezentacji będzie sukcesywnie publikowana od 15 lipca 2010 r. na stronie webowej

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Aby praca (dotyczy to także streszczenia, które powinno mieć tytuł w języku polskim i angielskim, słowa kluczowe w obydwu językach) przedstawiona w czasie konferencji mogła być opublikowana, jej tekst winien być przygotowany zgodnie z wymaganiami stawianymi artykułom drukowanym w czasopismach *Ecological Chemistry and Engineering* ser. A oraz S, które jest dostępne w wielu bibliotekach naukowych w Polsce i za granicą. Są one takie same dla prac drukowanych w półroczniku *Chemia – Dydaktyka – Ekologia – Metrologia*. Zalecenia te są również umieszczone na stronie webowej konferencji.

Koszt uczestnictwa w całej konferencji wynosi 1000 zł i pokrywa opłatę za udział, koszt noclegów i wyżywienia oraz rocznej prenumeraty Ecol. Chem. Eng. (razem blisko 2000 ss.) łącznie z materiałami Konferencji. Jest możliwość udziału tylko w jednym wybranym przez siebie dniu, wówczas opłata wyniesie 650 zł i będzie upoważniała do uzyskania wszystkich materiałów konferencyjnych, jednego noclegu i trzech posiłków (śniadanie, obiad, kolacja), natomiast osoby zainteresowane udziałem w dwóch dniach, tj. w pierwszym i drugim lub drugim i trzecim, winny wnieść opłatę w wysokości 800 zł. Opłata dla magistrantów i doktorantów oraz młodych doktorów biorących aktywny udział w Forum Młodych może być zmniejszone do 600 zł, przy zachowaniu takich samych świadczeń. Osoby te winny dodatkowo dostarczyć: rozszerzone streszczenia (4–6 stron) swoich wystąpień (**do 15.08.2010 r.**). Jest także wymagana opinia opiekuna naukowego. Sprawy te będą rozpatrywane indywidualnie przez Radę Naukową oraz Komitet Organizacyjny Konferencji. Członkowie Towarzystwa Chemii i Inżynierii Ekologicznej (z opłaconymi na bieżąco składkami) mają prawo do obniżonej opłaty konferencyjnej o 25 zł. Opłaty wnoszone po 15 września 2010 r. są większe o 10% od kwot podanych powyżej. Wszystkie wpłaty powinny być dokonane na konto w Banku Śląskim:

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Po konferencji zostaną wydane 4–6-stronicowe rozszerzone streszczenia wystąpień w półroczniku *Proceedings of ECOpole*. Artykuły te winny być przesłane do **1 października 2010 r**. Wszystkie nadsyłane prace podlegają zwykłej procedurze recenzyjnej. Wszystkie streszczenia oraz program Konferencji zostaną wydane na CD-ROM-ie, który otrzyma każdy z uczestników podczas rejestracji. Program będzie także umieszczony na stronie webowej Konferencji.

Prof. dr hab. Maria Wacławek
Przewodnicząca Komitetu Organizacyjnego
Konferencji ECOpole '10

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