

EFFECT OF DIFFERENT SULFUR DOSES AND FORMS ON CHANGES IN THE MINERAL NITROGEN CONTENT OF SOIL

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Abstract

Nitrogen, in particular nitrate nitrogen, is a mobile nutrient that can be readily dispersed in soil, thus causing environmental pollution. Sulfur may have a beneficial effect on nitrogen transformations in soil and in plants. The objective of this study was to determine the effect of sulfur fertilization on the dynamics of changes in mineral nitrogen (N-NH_4^+ and N-NO_3^-) content of soil samples collected each year in the spring and fall at a depth of 0-40 and 40-80 cm. A three-year field experiment was conducted in Byszwald near Lubawa. The soil had acidic reaction ($\text{pH}_{1 \text{ mol KCl dm}^{-3}}$ of 5.30) and contained the following concentrations of mineral nutrients: mineral nitrogen – 24.0, sulfate sulfur – 4.10, available phosphorus – 34.5, available potassium – 110.0 mg kg^{-1} soil. The experiment was carried out in a randomized block design and comprised eight fertilization treatments in four replications. Three sulfate sulfur (S-SO_4^{2-}) and elementary sulfur (S-S^0) fertilization levels were applied: 40, 80 and 120 kg ha^{-1} . The content of nitrate nitrogen (V) and ammonia nitrogen (III) was determined in soil samples by the colorimetric method using phenoldisulfonic acid and Nessler's reagent, respectively. In most cases, increasing sulfur doses caused an increase in the N-NH_4^+ content of soil samples collected at a depth of 0-40 cm. The N-NH_4^+ content of the 40-80 cm soil layer varied. NPK+S fertilization, in particular the application of a single S-SO_4^{2-} dose, contributed to an increase in N-NO_3^- concentrations in both sampled soil horizons in the majority of treatments, compared with the NPK treatment.

Key words: fertilization, sulfate sulfur, elementary sulfur, ammonia nitrogen, nitrate nitrogen, soil.

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WPLYW RÓŻNYCH DAWEK I FORM SIARKI NA ZMIANY ZAWARTOŚCI AZOTU MINERALNEGO W GLEBIE

Abstrakt

Azot, szczególnie forma azotanowa, należy do grupy tzw. pierwiastków mobilnych w glebie, może szybko rozpraszać się w naturalnym środowisku powodując jego zanieczyszczenie. Siarka może korzystnie wpływać na przemiany azotu w glebie i roślinie. Celem doświadczenia była ocena wpływu nawożenia siarką na dynamikę mineralnych form azotu (N-NH_4^+ , N-NO_3^-) w glebie, z poziomu 0-40 i 40-80 cm, pobieranej wiosną i jesienią w każdym roku. Badania przeprowadzono w 3-letnim doświadczeniu polowym w Byszwałdzie, w pobliżu Lubawy. Gleba wyjściowa miała odczyn kwaśny ($\text{pH}_{1 \text{ mol KCl dm}^{-3}}$ wynosiło 5,30), a zawartość składników mineralnych wynosiła: azot mineralny 24,0, siarka siarczanowa 4,10, przyswajalny fosfor 34,5 i potas 110,0 mg kg^{-1} gleby. Doświadczenie stałe założone metodą losowanych bloków obejmowało 8 obiektów nawozowych w 4 powtórzeniach. Zastosowano 3 poziomy nawożenia siarką: 40, 80 i 120 kg ha^{-1} w formie siarczanowej (S-SO_4^{2-}) i elementarnej (S-S^0). W przygotowanych próbkach glebowych oznaczono azot azotanowy (V) metodą kolorymetryczną z użyciem kwasu fenolodisulfonowego; azot amonowy (III) metodą kolorymetryczną z zastosowaniem odczynnika Nesslera. W poziomie gleby 0-40 cm wzrastające dawki siarki spowodowały na ogół zwiększenie zawartości N-NH_4^+ . W warstwie 40-80 cm zmiany zawartości N-NH_4^+ w glebie nie podlegały określonym prawidłowościom. W większości obiektów nawożenie NPK + S, szczególnie pojedynczą dawką S-SO_4^{2-} , przyczyniło się do zwiększenia zawartości N-NO_3^- w obydwu warstwach gleby w porównaniu z obiektem NPK.

Słowa kluczowe: nawożenie, siarka siarczanowa, siarka elementarna, azot amonowy, azot azotanowy, gleba.

INTRODUCTION

Optimal rates of sulfur-based fertilizers contribute to improving the utilization of nutrients, in particular nitrogen. The beneficial effect of sulfur on nitrogen transformations and the sulfur to nitrogen ratio has been demonstrated for example by SCHUNG et al. (1993), FISMES et al. (2000), KOZŁOWSKA (2002), KACZOR, BRODOWSKA (2002). Sulfur reduces the content of undesirable and harmful compounds, including nitrate nitrogen and ammonia nitrogen, in plants. Sulfur deficiency inhibits protein synthesis, disturbs the process of photosynthesis and leads to the accumulation of non-protein nitrogen (ZHAO et al. 1997, McGRATH et al. 1996, SCHERER 2001). Nitrogen is known to affect soil fertility (BEDNAREK, RESZKA 2008). Since nitrogen, in particular nitrate nitrogen, is a mobile nutrient, it can be readily dispersed in soil, thus causing environmental pollution and groundwater contamination (ARMSTRONG, BURT 1993, BOROWIEC, ZABŁOCKI 1996). Due to a steady increase in commercial crop production and related environmental issues, relationships between nitrogen and sulfur compounds in soil remain an important consideration.

The objective of this study was to determine the effect of increasing doses of sulfate sulfur and elementary sulfur on the content of mineral nitrogen compounds in soil samples collected at a depth of 0-40 and 40-80 cm.

MATERIAL AND METHODS

The effect of sulfur fertilization on the dynamics of changes in mineral nitrogen (N-NH_4^+ and N-NO_3^-) content of soil samples collected at a depth of 0-40 and 40-80 cm was studied. A three-year field experiment was conducted in Byszwałd near Lubawa, in 2000-2002. The soil had acidic reaction ($\text{pH}_{1 \text{ mol KCl dm}^{-3}}$ of 5.30) and contained the following concentrations of mineral nutrients: mineral nitro, gen – 24.0, sulfate sulfur – 4.10, available phosphorus – 34.5, available potassium – 110.0 mg kg^{-1} soil. The experiment was carried out in a randomized block design and comprised eight fertilization treatments in four replications: 1) 0; 2) NPK; 3) NPK + $\text{S}_1\text{-SO}_4^{2-}$; 4) NPK + $\text{S}_2\text{-SO}_4^{2-}$; 5) NPK + $\text{S}_3\text{-SO}_4^{2-}$; 6) NPK + $\text{S}_1\text{-S}^0$; 7) NPK + $\text{S}_2\text{-S}^0$; 8) NPK + $\text{S}_3\text{-S}^0$. Three sulfate sulfur (S-SO_4^{2-}) and elementary sulfur (S-S^0) fertilization levels were applied: 40, 80 and 120 kg ha^{-1} .

The following fertilizers were used: nitrogen – ammonium salt peter or ammonium sulfate, phosphorus – triple superphosphate, potassium – 60% potash salt or potassium sulfate, sulfur – potassium sulfate + ammonium sulfate and elementary sulfur in the treatments with this form of sulfur. The tested crops were common cabbage, onion and spring barley. The above plants were selected based on their sulfur requirements and sensitivity.

Soil samples were collected in each plot, at a depth of 0-40 cm and 40-80 cm, before setting up the experiment, after harvest of each crop and prior to the sowing of the next crop. In the spring of 2001, soil samples were collected only from the 0-40 cm soil layer due to persistent precipitation. Air-dried soil samples were passed through a 1 mm mesh sieve. The content of nitrate nitrogen (V) and ammonia nitrogen (III) was determined in soil samples by the colorimetric method using phenoldisulfonic acid and Nessler's reagent, respectively. The results were verified statistically with analysis of variance for two-factorial experiments in a randomized block design. Experimental factor *a* was sulfur form, and experimental factor *b* – sulfur dose. Regression analysis was performed using Statistica 6.0 PL software. The significance of differences between datasets was determined with Duncan's test.

RESULTS AND DISCUSSION

In the fall, after cabbage harvest, the ammonia nitrogen content of soil samples collected at a depth of 0-40 cm ranged from 0.30 to 3.30 mg kg^{-1} soil (Table 1). The application of a triple dose of elementary sulfur caused a significant increase in N-NH_4^+ concentrations, in comparison with the remaining sulfur doses. In the spring of 2001, a considerable increase in the ammonia nitrogen content of soil was noted, compared with the samples

Table 1

Effect of different rates and forms of sulfur on the content of ammonium nitrogen in soil (0-40 cm) (mg kg^{-1} soil)

Treatment	After cabbage harvest	Before onion sowing	After onion harvest	Before barley sowing	After barley harvest
0	0.30	39.8	6.40	7.50	4.40
NPK	2.40	12.8	4.90	5.40	4.50
NPK+ S ₁ -SO ₄ ²⁻	2.70	18.8	3.90	6.40	2.90
NPK+ S ₂ -SO ₄ ²⁻	0.40	25.8	5.00	14.0	4.10
NPK+ S ₃ -SO ₄ ²⁻	0.30	28.7	6.50	9.00	7.10
NPK+S ₁ -S ⁰	2.60	22.0	4.90	17.3	4.00
NPK+S ₂ -S ⁰	2.60	20.7	6.40	8.0	5.40
NPK+S ₃ -S ⁰	3.30	26.3	4.70	12.5	6.50
LSD- <i>p</i> -0.05					
<i>a</i>	0.080	1.190	0.260	0.420	0.320
<i>b</i>	0.110	1.680	0.360	0.600	0.450
<i>a x b</i>	0.160	2.380	0.510	0.850	0.630

SO₄²⁻ – sulfate sulfur; S⁰ – elementary sulfur; S₁ – 40 kg ha⁻¹, S₂ – 80 kg ha⁻¹, S₃ – 120 kg ha⁻¹, *a* – form of sulfur; *b* – dose of sulfur; *a x b* interaction, n.s. – no significant difference

analyzed in the fall. After harvest in 2001, the application of increasing sulfur doses led to an increase in the ammonia nitrogen content of soil, except in the treatment fertilized with 120 kg elementary sulfur. Soil samples collected in the spring of 2002 were characterized by a higher ammonia nitrogen content than the samples analyzed in the fall. Both the dose and form of sulfur had a significant effect on changes in N-NH₄⁺ levels. In the third year of the experiment, elementary sulfur exerted a stronger effect, which could have resulted from its oxidation to sulfate (ZHOU et al. 2002, SKWIERAWSKA, ZAWARTKA 2009). In the fall, after barley harvest, a decrease in the ammonia nitrogen content of the 0-40 cm soil layer was observed, in comparison with the same treatments studied in the spring. N-NH₄⁺ concentrations were in the range of 2.90-7.10 mg kg⁻¹ soil. Soil samples collected each year in the spring (at a depth of 0-40 cm) were found to accumulate larger quantities of N-NH₄⁺ than the samples collected in the fall of the preceding year. In most cases, increasing sulfur doses contributed to an increase in the N-NH₄⁺ content of soil after harvest, which was particularly noticeable in the second and third year of the study. In a laboratory experiment, the application of elementary sulfur significantly reduced the leaching of water-soluble ammonia nitrogen (ZAWARTKA, SKWIERAWSKA 2005). The N-NH₄⁺ content of the 40-80 cm soil layer varied (Table 2).

Table 2

Effect of different rates and forms of sulfur on the content of ammonium nitrogen in soil (40-80 cm) (mg kg^{-1} soil)

Treatment	After cabbage harvest	Before onion sowing	After onion harvest	Before barley sowing	After barley harvest
0	4.10	-	20.9	4.18	2.70
NPK	3.50	-	29.8	8.40	4.50
NPK+ S ₁ -SO ₄ ²⁻	2.20	-	24.3	4.57	3.50
NPK+ S ₂ -SO ₄ ²⁻	2.40	-	29.3	4.13	3.90
NPK+ S ₃ -SO ₄ ²⁻	3.50	-	29.0	4.56	4.80
NPK+S ₁ -S. ⁰	2.10	-	28.8	4.57	6.80
NPK+S ₂ -S. ⁰	3.60	-	25.0	5.87	4.30
NPK+S ₃ -S. ⁰	3.90	-	22.8	5.00	5.20
LSD- <i>p</i> -0.05					
<i>a</i>	0.080		0.720	n.s.	0.150
<i>b</i>	0.120	-	1.020	0.468	0.220
<i>a</i> x <i>b</i>	0.160		1.450	0.662	0.300

Explanation see Table 1.

In the fall, after cabbage harvest, the N-NO₃⁻ content of soil samples collected at a depth of 0-40 cm ranged from 2.60 to 6.20 mg kg^{-1} soil (Table 3). The highest N-NO₃⁻ content was noted in the treatment fertilized with 80 kg elementary sulfur. In the spring, before onion sowing, a significant increase in the N-NO₃⁻ content of soil was observed, in comparison with the same treatments studied in the spring, in particular after the application of 120 kg sulfate and elementary sulfur. Both the dose and form of sulfur had a significant effect on changes in N-NO₃⁻ levels. After the harvest in 2001, the N-NO₃⁻ content of soil decreased, which could have been due to its leaching out and uptake by plants. Similar results were reported by MARCINKOWSKI (1996) and SYKUT (2000). In the spring, prior to spring barley sowing, a substantial increase in the nitrate nitrogen of soil was noted, compared with the samples collected in 2000 and 2001, in particular in the treatment fertilized with a triple dose of elementary sulfate, which oxidized over time. In the fall of 2002, after harvest, nitrate nitrogen concentrations fluctuated.

In the fall of 2000, in the 40-80 cm soil layer, nitrate nitrogen content was in the range of 2.60-3.90 mg kg^{-1} soil. Both the dose and form of sulfur had a significant effect on changes in N-NO₃⁻ levels. In the fall of 2001, the N-NO₃⁻ content of soil was higher than in the previous year, in particular in treatments fertilized with 40 and 120 kg S-SO₄²⁻ ha⁻¹. Soil samples analyzed in the spring and fall of 2002 were characterized by a considerably lower nitrate nitrogen content than the samples collected in the fall of 2001.

Table 3

Effect of different rates and forms of sulfur on the content of nitrate nitrogen in soil (0-40 cm) (mg kg^{-1} soil)

Treatment	After cabbage harvest	Before onion sowing	After onion harvest	Before barley sowing	After barley harvest
0	2.60	9.20	2.00	11.0	10.6
NPK	5.30	6.30	2.50	14.7	14.2
NPK+ S ₁ -SO ₄ ²⁻	3.10	10.80	5.20	19.5	17.2
NPK+ S ₂ -SO ₄ ²⁻	5.00	7.50	5.80	19.8	16.8
NPK+ S ₃ -SO ₄ ²⁻	4.30	11.8	3.70	18.4	14.5
NPK+S ₁ -S ⁰	3.70	5.00	3.40	14.5	12.7
NPK+S ₂ -S ⁰	6.20	8.40	4.20	13.0	11.6
NPK+S ₃ -S ⁰	3.00	18.5	2.90	25.2	12.3
LSD- <i>p</i> -0.05					
<i>a</i>	0.110	0.72	n.s.	1.360	0.900
<i>b</i>	0.160	1.02	0.500	1.920	1.270
<i>a x b</i>	0.230	1.44	0.700	2.710	1.800

Explanation see Table 1.

Soil samples collected at a depth of 0-40 cm in NPK+S treatments were found to accumulate less of nitrates in the fall than in the spring (Table 3). In soil samples collected from the 40-80 cm layer, nitrate concentrations were higher in the fall (Table 4). As demonstrated by IGRAS and JADCZYŹYŹYN (2008), the risk of nitrate leaching is the greatest in the fall, due to precipitation. The decrease in N-NO_3^- concentrations in samples collected from the deeper soil layer in the spring could be related to translocation of nitrate nitrogen to groundwater. High mobility of nitrate ions was also observed by ZAWARTKA, SKWIERAWSKA (2004) in a lysimetric experiment.

No regular, unambiguous correlations between the form and dose of sulfur and nitrate concentrations in the soil were observed throughout the experiment. Nevertheless, NPK+S fertilization, in particular the application of a single S-SO_4^{2-} dose, contributed to an increase in N-NO_3^- concentrations in both sampled soil horizons in the majority of treatments, compared with the NPK treatment. The noted differences were statistically significant, as shown by the results of Duncan's test (Table 5).

In the spring and fall of 2000 and 2002, the predominant form of mineral nitrogen that accumulated in the 0-40 cm soil layer was N-NO_3^- . According to some authors (FOTYMA, KRYSZKOWSKA 1990, MOSIEJ, TUSIŹSKI 1993), higher nitrate content of deeper soil horizons results from high mobility of nitrate nitrogen in soil, particularly between the fall and spring, and from the antagonist effect of sulfate anions. In 2001, the predominant form of mineral

Table 4

Effect of different rates and forms of sulfur on the content of nitrate nitrogen in soil (40-80 cm) (mg kg^{-1} soil)

Treatment	After cabbage harvest	Before onion sowing	After onion harvest	Before barley sowing	After barley harvest
0	2.80	-	5.80	3.40	2.00
NPK	3.90	-	3.30	5.35	3.70
NPK+ S ₁ -SO ₄ ²⁻	3.00	-	28.5	3.85	4.00
NPK+ S ₂ -SO ₄ ²⁻	2.60	-	18.5	4.85	3.30
NPK+ S ₃ -SO ₄ ²⁻	2.90	-	20.5	6.22	5.90
NPK+S ₁ -S ⁰	2.90	-	16.0	4.75	2.50
NPK+S ₂ -S ⁰	3.40	-	12.7	5.20	2.30
NPK+S ₃ -S ⁰	3.80	-	7.80	3.42	3.10
LSD- <i>p</i> -0.05					
<i>a</i>	0.060		n.s.	n.s.	n.s.
<i>b</i>	0.090	-	1.740	n.s.	0.310
<i>a x b</i>	0.130		2.46	1.454	0.430

Explanation see Table 1.

Table 5

Significance of differences in the content of nitrate nitrogen in soil between particular objects according to Duncan's test.

Differences statistically significant at ($p \leq 0.05$)

Treatment	0	NPK	I-S-SO ₄ ²⁻	II-S-SO ₄ ²⁻	III-S-SO ₄ ²⁻	I-S-S ⁰	II-S-S ⁰	III-S-S ⁰
0								
NPK	0.537							
S ₁ -SO ₄ ²⁻	0.002*	0.014*						
S ₂ -SO ₄ ²⁻	0.023*	0.086	0.437					
S ₃ -SO ₄ ²⁻	0.013*	0.055	0.564	0.799				
S ₁ -S ⁰	0.297	0.620	0.046*	0.196	0.136			
S ₂ -S ⁰	0.256	0.549	0.058	0.228	0.163	0.883		
S ₃ -S ⁰	0.044*	0.140	0.308	0.763	0.604	0.290	0.326	
\bar{x}	5.922	6.688	10.107	9.075	9.390	7.302	7.484	8.702

Explanation see Table 1;

* \bar{x} average content of nitrate nitrogen in soil in particular objects for the years 2000-2003 (mg kg^{-1} soil).

nitrogen in both sampled soil layers was N-NH_4^+ . The above is consistent with the findings of SKOWROŃSKA (2004), who reported that in her study ammonia nitrogen had the highest share of total mineral nitrogen content.

CONCLUSIONS

1. In most cases, increasing sulfur doses caused an increase in the N-NH_4^+ content of soil samples collected at a depth of 0-40 cm. The N-NH_4^+ content of the 40-80 cm soil layer varied.

2. NPK+S fertilization, in particular the application of a single S-SO_4^{2-} dose, contributed to an increase in N-NO_3^- concentrations in both sampled soil horizons in the majority of treatments, compared with the NPK treatments.

3. The predominant form of mineral nitrogen that accumulated in soil (0-40 cm) was nitrate nitrogen in 2000 and 2002, and ammonia nitrate in 2001.

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