Fluctuations of nitrogen levels in soil profile under conditions of a long-term fertilization experiment

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ABSTRACT

The present study is focused on the correlation between varied long-term fertilization and changes in soil nitrogen concentrations. It was found that all fertilization systems significantly increased the levels of total, mineral and organic nitrogen in the soil profile. Organic fertilizers (manure and slurry) contributed to a more considerable increase in the concentrations of total nitrogen and nitrogen undergoing hydrolysis in 6M HCl, compared to mineral fertilizers. Ammonia nitrogen dominated over nitrate nitrogen among mineral nitrogen forms. Organic fertilization contributed to nitrate nitrogen accumulation, while mineral fertilization to ammonia nitrogen storage. The highest accumulations of nitrate nitrogen and ammonia nitrogen were observed after the application of slurry and manure, respectively. Hydrolyzable nitrogen content and its proportion in total nitrogen generally decreased with soil depth. An increase in the levels of organic nitrogen forms, i.e. nitrogen contained in amino sugars and amino acids as well as ammonia nitrogen from decomposition of amides, amino sugars and amino acids, was conditioned primarily on the application of organic fertilizers, particularly manure. Amino acid-N dominated among hydrolyzable nitrogen compounds (77%), while amino sugar-N accounted for 5.6% only.

Keywords: soil; fertilization; mineral and organic nitrogen forms

Nitrogen is one of the major nutrients affecting soil fertility (Heumann et al. 2002). The content of various forms of this element in the soil depends primarily on the processes of immobilization and organic matter mineralization. The soil levels of nitrogen forms available to plants are generally low, and they range from 1 to 5% (Bednarek and Tkaczyk 2002). A gradual depletion of the available nitrogen pool is observed in agricultural ecosystems as a consequence of ammonium and nitrate ion uptake by crops and soil microbes (Deng et al. 2000). Organic nitrogen is usually bound to clay and humus particles known as soil colloids, forming stable complexes. Organic compounds unavailable to plants undergo constant changes whose direction and rate depend mainly on soil biological activity and fertilizer type (Smith and Poul 1990, Schmidt et al. 2000).

The objective of this study was to analyze the pattern of nitrogen mineralization on Haplic Luvisol under conditions of three long-term fertilization systems: organic, mineral and organic-mineral.

MATERIAL AND METHODS

Changes in soil nitrogen content were determined based on a long-term fertilization experiment established in 1972 on Haplic Luvisol developed from heavy loamy silty sand underlain by light loam. The effect of organic (manure and slurry at two rates) and mineral (NPK) fertilizers was compared in the experiment. Slurry rate I and the rates of manure and mineral fertilizers were equivalent in terms of total nitrogen amount. Slurry rate II was equivalent to manure in terms of organic carbon amount. In the slurry treatment with rate II, average per year introduced an increase of nitrogen by 56 kg per one hectare (rate I – 156 kg N, rate II – 212 kg N/ha). Apart from the organic fertilization vari-

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ant, organic fertilizers were applied together with complementary mineral fertilizers (PK), in some treatments at half the rate introduced into the soil in plots with mineral fertilization. The following crop rotations were used: potato, spring barley + undersown red clover with grasses, red clover with grasses, winter rape, winter wheat + rye as a winter catch crop, silage maize, spring barley, winter wheat. Clover with grasses were grown only in the first two cycles of crop rotations.

This paper presents experimental results obtained in 2003–2005 (means of three years). Each year after harvest soil samples were taken at four levels of the soil profile: 0–25, 26–50, 51–75, 76–100 cm. Total nitrogen content was determined by the Kjeldahl method. Mineral nitrogen was extracted with a 1% K_2SO_4 solution. The extracted ammonia nitrogen was determined by a colorimetric method with Nessler reagent. Nitrate nitrogen was determined by a spectrophotometric method. Organic nitrogen fractions were determined in two soil layers, 0–25 and 26–50 cm, by the Keeney and Bremner method, during hydrolysis in 1M and 6M HCl solutions. Hydrolyzable nitrogen was determined by distillation with a K_2SO_4 catalyzing mixture, while nitrogen contained in amino acids was determined by distillation with borate buffer. Nitrogen contained in amino sugars was calculated as the difference between the amount of ammonia nitrogen distilled from the hydrolyzate with MgO and distilled after the addition of borate buffer (Page et al. 1982).

The results were processed statistically by a two-factorial analysis of variance using STATISTICA ver. 6 software. The least significant differences (LSD) were determined at the significance level of $P = 0.05$.

RESULTS AND DISCUSSION

Nitrogen has a profound effect on soil fertility and crop yield. This nutrient contributes to an increase in yield and after-harvest residue, thus preventing the loss of soil organic matter (Wiater and Chwil 2005). The main sources of soil nitrogen are organic and mineral fertilizers (Flessa et al. 2000, Garz et al. 2000, Merbach et al. 2000).

In our study the average total nitrogen content of soil depended on the type and rate of fertilizers. All fertilization systems had a highly significant effect on an increase of the nitrogen content in the soil profile (Table 1).

Over the entire experimental period the highest mean increase in total nitrogen content (0.27 g/kg as compared to the control) was observed in the uppermost soil layer. Soil nitrogen content decreased with soil depth. In treatments where balanced nitrogen rates were applied, manure was found to have the greatest impact on an increase in the nitrogen content of the soil profile. The beneficial influence of manure was also reported by Sosulski and Łabętowicz (2006). The least positive effect was noted in case of mineral fertilizers. The in-

Table 1. Total nitrogen content of Haplic Luvisol (g/kg) (mean of 3 years)

Number	Fertilizers	Depth (cm)				
		0–25	26–50	51–75	76–100	mean
I	without fertilization	0.58	0.42	0.21	0.11	0.33
II	slurry rate I	0.73	0.51	0.31	0.16	0.43
III	slurry rate I + PK	0.76	0.56	0.37	0.24	0.48
IV	slurry rate II	0.84	0.64	0.44	0.30	0.56
V	slurry rate II + PK	0.92	0.70	0.49	0.34	0.61
VI	farmyard manure (FYM)	0.94	0.74	0.40	0.27	0.59
VII	FYM + PK	1.09	0.80	0.62	0.40	0.73
VIII	NPK	0.71	0.41	0.24	0.18	0.39
$LSD_{0.05}$						
fertilizers				0.04		
soil depth				0.03		
interactions				0.08		

Table 2. Mineral nitrogen content of Haplic Luvisol (mg/kg) (mean of 3 years)

Number	Fertilizers	Depth (cm)				
		0–25	26–50	51–75	76–100	mean
I	without fertilization	9.4	7.0	6.2	3.6	6.5
II	slurry rate I	16.3	11.9	7.4	5.6	10.3
III	slurry rate I + PK	21.1	15.6	10.1	7.6	13.6
IV	slurry rate II	23.3	18.4	12.2	9.7	15.9
V	slurry rate II + PK	22.3	18.7	11.9	9.5	15.6
VI	farmyard manure (FYM)	27.6	21.4	15.1	13.5	19.4
VII	FYM + PK	34.3	24.1	16.6	14.1	22.3
VIII	NPK	17.1	11.0	8.5	7.3	10.9
$LSD_{0.05}$						
fertilizers				1.2		
soil depth				0.9		
interactions				2.5		

fluence of slurry rate II was less desirable than that of manure, especially in the uppermost soil layer and subsoil (0–25 cm and 26–50 cm), since in deeper layers the effect of these fertilizers was comparable. Therefore, it may be concluded that both fertilizers promoted nitrogen translocation into deeper soil layers, which could result in the migration of this nutrient to waters. The application of mineral fertilizers (PK) in combination with organic fertilizers enabled to increase the nitrogen content of soil by 15% on average. The best results were achieved when mineral fertilizers were combined with farmyard manure.

Among various nitrogen forms, ammonia nitrogen and nitrate nitrogen play the most important role when seen from the ecological perspective. Their concentrations in the soil provide a basis for determining optimal fertilization levels. The amount of mineral nitrogen available to plants depends, among others, on the type and rate of fertilizers (Schmidt et al. 2000).

The mineral nitrogen content of soil varied depending on the applied fertilizers (Table 2). Similar dependencies were also described by Sainju et al. (2002). Compared to the control treatment, an increase in the content of this nitrogen form in the surface layer of soil was equal to 145%. Mineral nitrogen content decreased with soil depth. A comparison of the fertilizers that supplied the same amount of nitrogen shows that the most beneficial effect was recorded for manure, followed by NPK. In the majority of treatments complementary mineral fertilization (PK) combined with organic fertilization contributed to an increase in the mineral nitrogen content of soil.

In the temperate climate zone the dominant form of mineral nitrogen is usually ammonia nitrogen, which was also confirmed by the present study (Figure 1). Manure application contributed to ammonia nitrogen accumulation, which suggests that organic nitrogen compounds introduced with this fertilizer were converted into ammonia nitrogen as a result of microbiological changes. The effect of mineral fertilizers (PK) applied together with organic fertilizers was ambiguous. When applied with slurry rate I and manure, these fertilizers caused an increase in the ammonia nitrogen content of the soil profile. However, when combined with slurry rate II they caused a decrease in the content of this nitrogen form. Rate II of slurry caused higher accumulation of ammonia nitrogen for 0.13 $N\text{-}NH_4$ than rate I.

If not utilized by plants, ammonia nitrogen undergoes nitrification and is converted into nitrate nitrogen (Bednarek and Tkaczyk 2002). All three fertilization systems applied in this experiment contributed to an increase in the average content of this form of mineral nitrogen in the soil (Figure 1).

Compared to the control treatment, a mean increase in the nitrate nitrogen content in topsoil in fertilized treatments was 4.5 mg/kg. The content of this nitrogen form decreased with soil depth, which was most probably related to lower

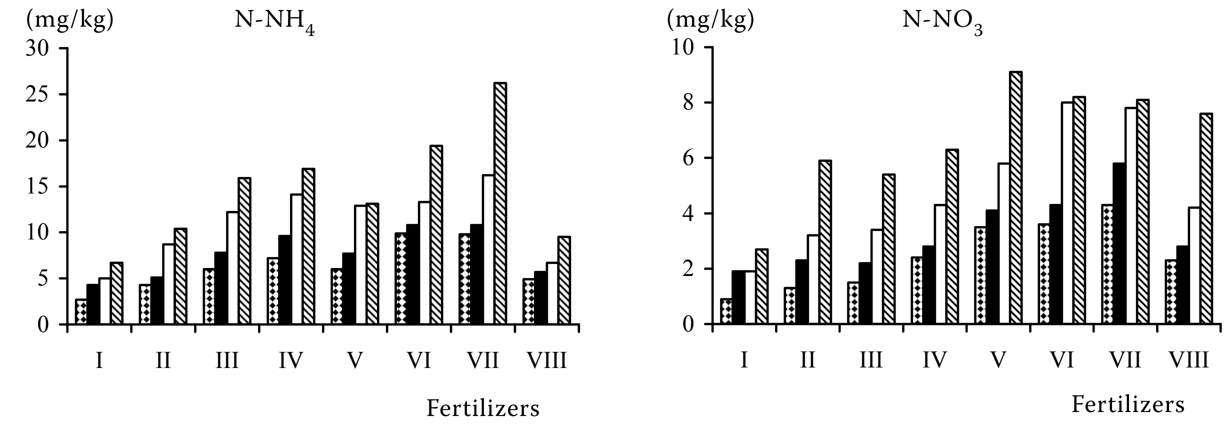


Figure 1. Average content of ammonia nitrogen and nitrate nitrogen in the soil (mg/kg)
$N\text{-}NH_4$ – $LSD_{0.05}$ for: fertilizers 0.8, soil depth 0.6, interactions 1.7
$N\text{-}NO_3$ – $LSD_{0.05}$ for: fertilizers 0.4, soil depth 0.3, interactions 0.8
For fertilizers see explanations in Table 1; the bars from the left: 76–100, 51–75, 26–50, 0–25

nitrification efficiency (Heumann et al. 2002). However, the effect of fertilization was noticeable even at the depth of 1 m, where it caused more than a threefold increase in nitrogen content, compared to the control. A comparison of different fertilizers containing an identical amount of nitrogen shows that manure application caused the highest mean increase in the nitrogen content of the soil profile (by 4.1 mg/kg on average). Mineral fertilization contributed to a higher concentration of nitrate nitrogen, compared to slurry rate I. As regards organic fertilizers equivalent in terms of organic carbon amount, nitrate nitrogen content was found to be significantly higher in manured soil than in soil fertilized with slurry rate II. The mean difference in the average $N\text{-}NO_3$ content in the analyzed treatments was 2.0 mg/kg. Mineral fertilization (PK) combined with organic fertilization affected an increase in the content of this nitrogen form, compared to treatments in which only organic fertilizers were applied.

Both the present results and literature data confirm the complex nature of mineral nitrogen changes in the soil, as well as the fact that fertilizers, if properly applied, are among the major factors affecting these changes (Borken and Matzner 2004, Heumann and Böttcher 2004).

Organic nitrogen constitutes a mixture of different compounds – components of microbial biomass, after-harvest residues and organic fertilizers. The intensity of mineralization may vary widely (Heumann et al. 2002). An accelerated and uncontrolled rate of this process can result in the release of excess mineral nitrogen, exceeding the nutrient requirements of plants.

It was found that on average 87% of total nitrogen undergoes hydrolysis in a 6M HCl solution. The use of a weaker solvent, i.e. a 1M HCl solution, reduced the amount of hydrolyzed nitrogen by 14% on average (Figure 2).

All fertilization systems applied in this experiment contributed to an increase in the content of hydrolyzable nitrogen, in comparison with the control treatment (Figure 2). The increase in the content of nitrogen extracted with 6M HCl caused by long-term manure application was by 33, 48 and 14% significantly higher, compared to fertilization with slurry rate I, NPK and slurry rate II, respectively (Figure 2). Mineral fertilizers (PK) caused a more significant increase in hydrolyzable nitrogen content than organic fertilizers. Both the content of the above nitrogen form and its proportion in total N were the highest in the surface soil layer, and gradually decreased with soil depth.

The first stage of mineralization is ammonification, during which organic nitrogen is converted into amino acids and amino sugars (Heumann et al. 2002). Bednarek and Tkaczyk (2002) demonstrated that the above forms of organic nitrogen undergo mineralization at the fastest rate among all organic compounds containing nitrogen. Since amino acids and amino sugars are readily decomposed and assimilated by microorganisms, they are not very persistent in the soil. As regards their availability for plant uptake, they take the second position after mineral nitrogen forms.

Amino acid-N dominated among hydrolyzable nitrogen compounds, accounting for 86% of N hydrolyzed with 1M HCl and 77% of N hydrolyzed with 6M HCl, while amino sugar-N made up only 2% and

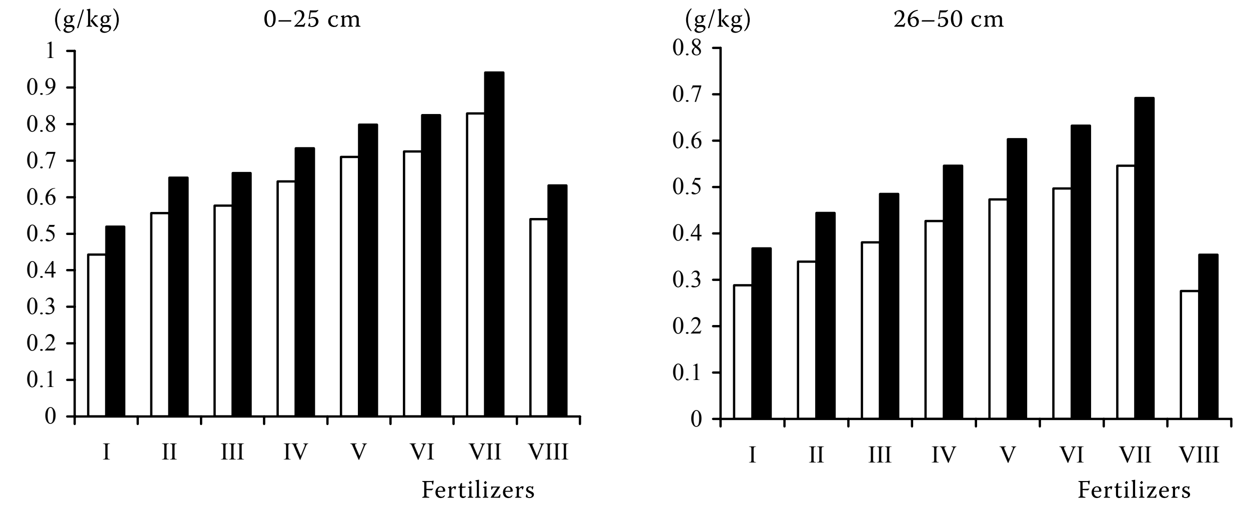


Figure 2. Average content of hydrolyzable nitrogen in the soil (g/kg)
N-NH_4 – $LSD_{0.05}$ for: fertilizers 0.04, hydrolysis solutions 0.07, interaction 0.03
N-NO_3 – $LSD_{0.05}$ for: fertilizers 0.03, hydrolysis solutions 0.08, interaction 0.02
For fertilizers see explanation in Table 1; the bars from the left: 1M HCl, 6M HCl

5%, respectively (Figure 3). Dying microorganisms reduce the rate of mineralization of amino acids and amino sugars, and part of organic nitrogen is released as NH_4^+ of unknown origin. This ion may be released into the atmosphere as ammonia or accumulated in the soil as an ammonium ion. In the present study nitrogen of unknown origin accounted for 14.5% and 14% of total nitrogen hydrolyzed in 1M HCl and 6M HCl, respectively.

The intensity of nitrogen release varied. The identification of chemical structures of organic nitrogen molecules revealed a significant effect of the applied fertilizers on the form of organic nitrogen bonds, as confirmed by Heumann and Böttcher (2004).

The content of organic nitrogen forms in the soil was significantly affected by the total nitrogen content of soil. All types of fertilization contributed to an increase in the content of all organic nitrogen forms, compared to the control (Figure 4). Long-term organic and organic-mineral fertilization caused a higher increase in the content of these nitrogen forms, in comparison with mineral fertilization, which is consistent with the results obtained by Heumann et al. (2002).

The highest increase in the content of amino acid-N and amino sugar-N was observed in manured soil. This indicates that the content of these nitrogen forms in the soil is dependent primarily on the supply of organic matter. Over the entire experimental period, the highest mean increase in the analyzed nitrogen forms was recorded in the uppermost soil layer. The content of both organic nitrogen forms decreased with soil depth.

The difference between total soil nitrogen content and hydrolyzable nitrogen content provided a basis

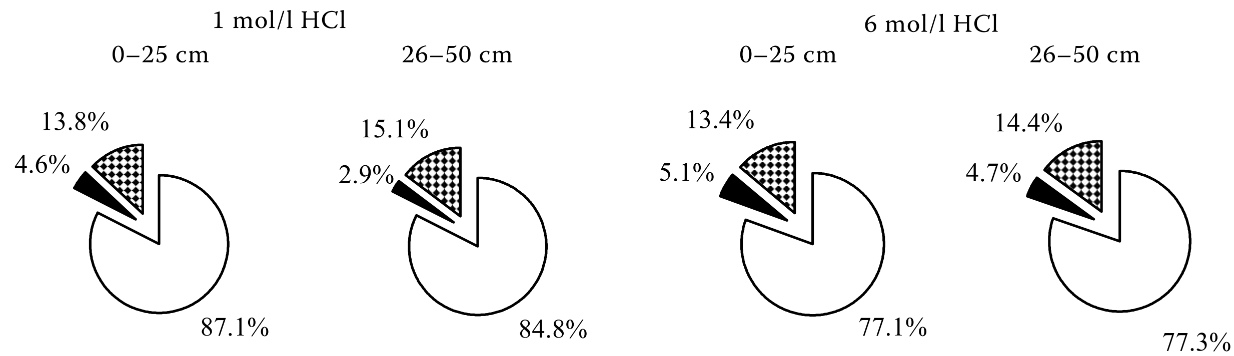
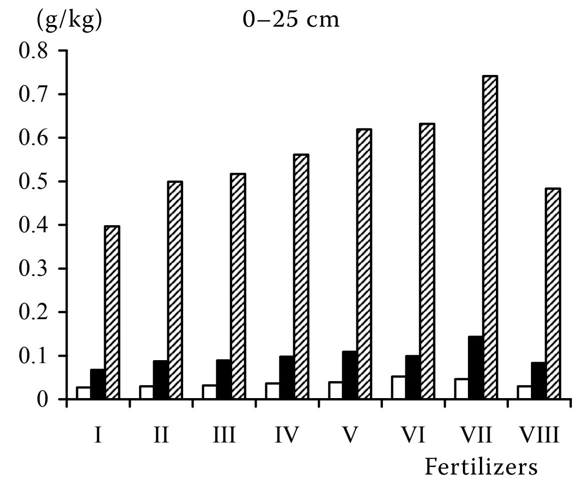


Figure 3. Percentage of organic nitrogen forms in hydrolyzable N (mean of all treatments)
□ amino acid-N, ■ amino sugar-N, ▩ N of unknown origin



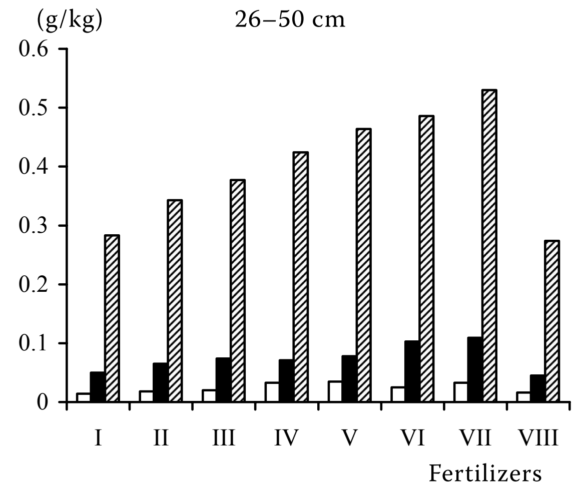


Figure 4. Average content of organic nitrogen forms in the soil (g/kg) (hydrolysis in 6M HCl)
The bars from the left: amino sugar-N, N of unknown origin, amino acid-N
For fertilizers see explanation in Table 1

for calculating the content of non-hydrolyzable nitrogen. This part of nitrogen has not been investigated in detail to date. Most probably it contains organic nitrogen compounds permanently bound to clay minerals. In the soil hydrolyzed with a 6M HCl solution it accounted for 13% of total nitrogen content on average. Manure equivalent to slurry in terms of both total nitrogen amount and total carbon amount caused the greatest accumulation of non-hydrolyzable N. Mineral fertilizers (PK) combined with organic fertilizers contributed to further accumulation of non-hydrolyzable nitrogen, whose content in the soil increased on average by 16% (6M HCl) and 9% (1M HCl), in comparison with organic fertilizers applied alone.

The applied fertilizers caused a significant increase in the total nitrogen content of soil, which ranged from 0.39 (g/kg) in the treatment fertilized with NPK to 0.73 (g/kg) in the treatment fertilized with manure + PK. Total nitrogen content decreased gradually with soil depth.

Mineral nitrogen content increased as a result of fertilization. Long-term organic fertilization increased mineral nitrogen content to a much greater degree than mineral fertilization. Slurry rate II, equivalent to manure in terms of organic carbon amount, contributed most to nitrate nitrogen accumulation. The highest concentration of ammonia nitrogen was recorded in manured soil.

Amino acid-N dominated among hydrolyzable nitrogen compounds, accounting for 86% of N hydrolyzed with 1M HCl and 77% of N hydrolyzed with 6M HCl, while amino sugar-N made up only 2% and 5%, respectively.

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