

The impact of long-term application of inorganic nitrogen fertilizers and manure on changes of selected properties of organic matter in sandy loam soil

Wpływ wieloletniego nawożenia azotem i obornikiem na zmiany wybranych właściwości materii organicznej gleby lekkiej

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Abstract

The aim of the research was to assess the effect of long-term application of different doses of nitrogen fertilizers with or without manure to changes in the total organic carbon content, total nitrogen content, evaluation of dissolved organic carbon content and the value of absorbance coefficient ($A_{4/6}$) in sandy loam soil. The base of research was the long-term field experiment, established in 1979 at the Wierzchucinek Experimental Station close to Bydgoszcz city - Poland. The experiment was carried out in the three-course crop rotation, potato, rye, rye in randomized split-plot design. The experimental treatments were four levels of N fertilizers in 0, 47, 93, and 140 kg·ha⁻¹·yr⁻¹ (N₀, N₁, N₂, N₃) as a 1st factor of experiment, and the same doses of N fertilizers with farmyard manure application (30 t·ha⁻¹) as a 2nd factor. After 36 years of experiment the content of total organic carbon was 26% lower and the content of total nitrogen 13% higher compared to the values determined before the experiment foundation (1979). The consequence of changes in the content of organic carbon and total nitrogen, are changes in the ratio of organic carbon content and total nitrogen content. It was noticed that the use of manure and different nitrogen doses resulted in a decrease of organic carbon content and total nitrogen content value. After application of different nitrogen doses, organic carbon content ranged from 122.4 to 152.2 mg·kg⁻¹. The same nitrogen doses applied simultaneously with farmyard manure increased the organic carbon content,

which ranged from 133.5 to 166.7 mg·kg⁻¹. The changes of the organic carbon content did not effect on percentage of this fraction in the total organic carbon. Percentage of organic carbon content in total organic carbon content was on averaged 1.6%. After the application of different nitrogen doses, humic acids of analyzed soils were characterized by lower average value of A_{4/6} (5.4). However, the application of nitrogen doses with manure brought a higher - 6.3 - A_{4/6} value. Farmyard manure application caused the formation of humic acids of lower molecular weight and a low humification degree.

Keywords: evaluation of dissolved organic carbon content, long-term experiment, manure, nitrogen doses, organic matter, total nitrogen content, total organic carbon content

Streszczenie

Celem pracy było zbadanie wpływu długookresowego nawożenia zróżnicowanymi dawkami azotu stosowanymi z obornikiem lub bez tego nawozu na zmiany zawartości ogólnego węgla organicznego (OWO), azotu ogółem (N_{og}), rozpuszczalnego węgla organicznego (RWO) w glebie oraz określenie wartości absorbancji (A_{4/6}). Podstawą badań było statyczne wieloletnie doświadczenie polowe, założona w 1979 roku w Stacji Badawczej w Wierzchucinku koło Bydgoszczy. Prowadzono je w trzyletnim, uproszczonym zmianowaniu: ziemniak – żyto ozime – żyto ozime. Pierwszym czynnikiem doświadczenia było zróżnicowane nawożenie azotem, dawki w kg·ha⁻¹·r⁻¹ wynosiły: N₀, N₄₇, N₉₃, N₁₄₀, drugim zastosowane dawki azotu na tle obornika (30 t·ha⁻¹). Po 36 latach stosowanego nawożenia średnie zawartości węgla oznaczone w próbkach glebowych były średnio niższe o 26%, natomiast zawartości azotu ogółem w glebie były wyższe o 13% w porównaniu do zawartości określonych w glebie przed założeniem doświadczenia (1979). Konsekwencją zmian zawartości węgla organicznego i azotu ogółem, są zmiany wartości stosunku zawartości węgla do azotu ogółem. Stosowanie łącznie obornika i zróżnicowanych dawek azotu spowodowało zawężenie wartości stosunku zawartości węgla do azotu ogółem. Stwierdzono, że zawartości węgla organicznego w glebie po zastosowaniu zróżnicowanych dawek azotu, wahały się w zakresie od 122.4 mg·kg⁻¹ do 152.2 mg·kg⁻¹ natomiast aplikacja azotu na tle obornika spowodowała, że zawartości te mieściły się w zakresie od 133.5 mg·kg⁻¹ do 166.7 mg·kg⁻¹. Zawartości węgla organicznego nie przełożyły się na procentowy udział tej frakcji w całkowitej zawartości węgla organicznego. Udział ten średnio wynosił 1.6%. Zauważono również, że po aplikacji badanych dawek azotu, kwasy huminowe analizowanych gleb charakteryzowały się średnio niższymi wartościami współczynnika A_{4/6}, który wynosił 5.4. Natomiast po zastosowaniu zróżnicowanych dawek azotu łącznie z obornikiem wynosił 6.3. Nawożenie obornikiem generowało powstawanie kwasów huminowych o mniejszej masie cząsteczkowej i o niskim stopniu humifikacji.

Słowa kluczowe: dawki azotu, doświadczenie wieloletnie, materia organiczna, obornik, zawartość azotu ogółem, zawartość rozpuszczalnego węgla organicznego, zawartość węgla ogółem

Introduction

Intensive long-term cultivation of soils including unbalanced fertilization, produces changes in their chemical properties. Moreover such procedures affect biological activity, acidification, lead to reduction of humus content and sorption capacity which in turn leads to the decrease of soil fertility (Jaskulska, 2003; Nardi et al., 2004; Haynes 2005; Mercik et al., 2005; Gregorich and Beare, 2007; Pałosz, 2009). Soil humus has complex chemical composition with specific properties, and is not protected against dissolution and leaching. Organic matter included humus, especially its organo-mineral associations, are recognized as the total organic carbon (TOC). This parameter as well as total nitrogen (TN) are treated as indicators of the changes in soil abundance and fertility. The determining factors of accumulation and transformation processes of TOC and TN are among others intensity of the applied tillage, mainly applied mineral and organic fertilizers (Blair et al., 2006; Constantin et al., 2010). In contrast, the dissolved organic matter fraction (DOM) is a sensitive indicator of changes in the soil environment. This fraction, expressed as the content of dissolved organic carbon (DOC), represents the most mobile hence accessible part of the soil organic matter (SOM), and also significantly depends on fertilization (Bolan et al., 2004; Haynes, 2005; Brookers et al., 2007).

As a result of this, research has been undertaken to determine the impact of the long-term application of varied doses of nitrogen with or without manure, on the changes in total carbon content (TOC), total nitrogen (NT), and dissolved organic carbon (DOC). An additional aspect of the study was to characterize humic acids by assessing the value of absorbance coefficient ($A_{4/6}$).

Materials and methods

The base of research was the long-term field experiment, established in 1979 at the Wierzchucinek Experimental Station of the UTP University of Science and Technology in Bydgoszcz (17°51'E, 53°13'N; Figure 1). The experiment was carried out in the three-course crop rotation, potato, rye, rye in randomized split-plot design in four replications (Figure 2, Table 1).

The experimental treatments were four levels of N fertilizers in 0, 47, 93 and 140 kg·ha⁻¹·yr⁻¹ (N₀, N₁, N₂, N₃) as a 1st factor of experiment, and the same doses of N fertilizers with farmyard manure (FYM) application (30 t·ha⁻¹) as a 2nd factor. The experiment was conducted on Albic Luvisols (IUSS 2014), formed from glacial till, with Ap, Et, Bt, BC, C horizon sequence in soil profile, and sandy loam (18% of clay) texture in ploughing horizon. According to Żarski et al. (2014), average annual precipitation on investigated area is 307.6 mm, and it is one of the lowest values in Poland. The multi-year average sums of precipitation and temperature (1981 - 2014) for Poland is 537 mm and 8 °C, respectively (Żarski et al., 2010). In 1979 the soil reaction was slightly acid (5.6 pH), with 6.63 g·kg⁻¹ of TOC and 119.4 mg·kg⁻¹ of DOC. The total nitrogen content (TN) and the content of available forms of P and K were: 0.78 g·kg⁻¹, 42.7 mg·kg⁻¹ and 62.3 mg·kg⁻¹ respectively.



Figure 1. Location of experimental station - kujawy pomeranian region – Poland

Rysunek 1. Lokalizacja stacji badawczej – woj. kujawsko-pomorskie - Polska

| | | | | | | | |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 32 | 31 | 30 | 29 | 28 | 27 | 26 | 25 |
| N ₀ | N ₁ | N ₂ | N ₃ | N ₀ | N ₁ | N ₂ | N ₃ |
| 24 | 23 | 22 | 21 | 20 | 19 | 18 | 17 |
| N ₁ | N ₀ | N ₂ | N ₃ | N ₀ | N ₂ | N ₃ | N ₁ |
| 16 | 15 | 14 | 13 | 12 | 11 | 10 | 9 |
| N ₁ | N ₂ | N ₃ | N ₀ | N ₂ | N ₃ | N ₁ | N ₀ |
| 8 | 7 | 6 | 5 | 4 | 3 | 2 | 1 |
| N ₃ | N ₂ | N ₀ | N ₁ | N ₃ | N ₂ | N ₀ | N ₁ |

■ – FYM application, □ – no FYM application, 1-32 – plot no, N₀-N₃ – nitrogen doses

■ – Nawożenie obornikiem, □ – bez nawożenia obornikiem, 1-32 – numery poletek, N₀-N₃ – dawki azotu

Figure 2. Scheme of experiment

Rysunek 2. Schemat doświadczenia

After the 12th rotation in 2015, soil samples were collected for analysis where the following parameters were determined:

- total organic carbon content (TOC) by sulfochromic wet oxidation method in the potassium dichromate solution - K₂Cr₂O₇ (ISO 14235, 1998),
- total nitrogen content (TN) – Kjeldahl method prior mineralization in concentrated H₂SO₄ in a ratio 1:2 soil: acid (Tecator Kjeltac System 1026 Distilling Unit, Denmark),

- dissolved organic carbon content (DOC) with the SKALAR TOCN FORMACS™ analyzer (Dębska and Gonet, 2002). Extraction with 0.004 M CaCl₂ from air dry samples was carried out for 1 h at the soil: extractant ratio of 1:10. DOC content was expressed in mg C·kg⁻¹ D.M. of soil sample and in % organic C.

Additionally, a determination of the optical properties of humic acids in the UV-VIS range, at wavelengths of 465 nm and 665 nm, was carried out using a Perkin-Elmer Lambda 20 spectrophotometer. On the basis of these values the value of the absorbance coefficient $A_{4/6}$ (Schnitzer and Khan, 1978) was calculated. The relationship between the measured parameters was calculated statistically using Tukey's test on Statistica10.0.

Table 1. Crop rotation and doses of fertilizers
Tabela 1. Zmianowanie i dawki zastosowanych nawozów

| Crop Zmianowanie | Dose of fertilization Dawki nawozów | | | | | |
|---------------------|--|-----|----------------|----------------|----------------|----------------|
| | P | K | N ₀ | N ₁ | N ₂ | N ₃ |
| Potato Ziemniaki | 35 | 100 | 0 | 60 | 120 | 180 |
| Rye Żyto | 35 | 66 | 0 | 40 | 80 | 120 |
| Rye Żyto | 35 | 83 | 0 | 40 | 80 | 120 |

Results and discussion

Long-term application of fertilizers is often the cause of changes in soil fertility, mainly in organic carbon (TOC) and total nitrogen (TN) (Slepetiene and Slepatys, 2005; Blair et al., 2006; Liu et al., 2006; Khalid et al., 2007).

Independently of fertilizing variant in 2015, the content of total organic carbon (TOC) in average was 26% lower in comparison to the values determined before the experiment foundation (1979-13 g·kg⁻¹). It was found that after the 36 years of the experiment TOC content was significantly determined by the applied nitrogen doses and the interaction of investigated factors (total nitrogen and total nitrogen with manure). After application of different nitrogen doses, the content of this parameter ranged from 8.07 to 10.38 g·kg⁻¹, however after fertilization with nitrogen and manure the content ranged from 7.06 to 11.49 g·kg⁻¹ (Table 2). These values are lower than the average value (12.8 g·kg⁻¹) for sandy soils in Poland (Stuczyński et al., 2007). The highest TOC values were found in the soil after the nitrogen application in dose

N₁ and N₃ with FYM, the lowest in N₀. Similar trends have been identified by other authors (Jaskulska, 2003; Blair et al., 2006; Sosulski and Korc, 2011).

Table 2. Investigated soil parameters (year 1979 and 2015)

Tabela 2. Badane cechy gleby (1979 i 2015 rok)

| Fertilization Nawożenie | | TOC OWO g·kg ⁻¹ | TN N _{og} g·kg ⁻¹ | TOC/TN OWO/N _{og} | DOC RWO mg·kg ⁻¹ | A _{4/6} |
|---|-----------------|----------------------------------|---|-------------------------------|-----------------------------------|------------------|
| 1979 Initial value Wartości początkowe | | 6.63 | 0.78 | 8.5 | 119.4 | - |
| | N ₀ | 8.07 ^c | 0.74 ^b | 10.9 | 122.4 | 5.13 |
| | N ₁ | 8.08 ^c | 0.79 ^{ab} | 10.2 | 142.5 | 5.54 |
| 2015 Without FYM Bez obornika | N ₂ | 10.38 ^a | 0.81 ^a | 12.8 | 140.9 | 5.37 |
| | N ₃ | 9.1 ^b | 0.85 ^a | 10.7 | 152.2 | 5.56 |
| | Mean Średnia | 8.9 [*] | 0.8 [*] | 11.6 | 139.5 [*] | 5.4 |
| | N ₀ | 7.06 ^b | 0.75 ^c | 9.4 | 133.5 | 6.17 |
| | N ₁ | 11.49 ^a | 0.96 ^b | 12 | 156.9 | 6.55 |
| 2015 With FYM Z obornikiem | N ₂ | 11.38 ^a | 0.97 ^b | 11.7 | 160.6 | 6.26 |
| | N ₃ | 11.45 ^a | 1.15 ^a | 10 | 166.7 | 6.25 |
| | Mean Średnia | 10.35 [*] | 0.96 [*] | 10.78 | 154.4 [*] | 6.3 |

* The mean values for the tested parameter in the column marked with * differ significantly depending on the applied manure doses (P<0.05), ^{a, b, c} the mean values for the tested parameter marked with different letters in the column differ significantly depending on the applied nitrogen doses (P<0.05), TOC - total organic carbon content; TN - total nitrogen content; DOC - dissolved organic carbon content; A_{4/6} - absorbance coefficient

* Wartości średnie dla badanego parametru umieszczone w kolumnie oznaczone * różnią się istotnie w zależności od aplikacji obornika (P<0.05), ^{a, b, c} wartości średnie dla badanego parametru umieszczone w kolumnie oznaczone ^{a, b, c} różnią się istotnie w zależności od aplikacji dawek azotu (P<0.05), OWO - ogólny węgiel organiczny; N_{og} - azot ogólny; RWO - rozpuszczalny węgiel organiczny; A_{4/6} - współczynnik absorpcji

Otherwise the content of total nitrogen (TN) was on average 13% higher compared to the values determined in 1979- $0.78 \text{ g}\cdot\text{kg}^{-1}$. The content of total nitrogen (TN) in the soil, following the application of different doses of nitrogen fertilizers (1st factor), ranged from 0.74 to $0.85 \text{ g}\cdot\text{kg}^{-1}$, and in the case of combined nitrogen/manure application (2nd factor), it ranged from 0.75 to $1.15 \text{ g}\cdot\text{kg}^{-1}$. The highest total nitrogen content in the soil was noted after the application of the highest dose of nitrogen N_3 ($140 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$) and manure ($30 \text{ t}\cdot\text{ha}^{-1}$).

It should be emphasized that, on average, both TOC and TN values were higher after the application of mineral nitrogen fertilizers with farmyard manure. Similar trends have been noticed by other authors (Jaskulska, 2003; Blair et al., 2006; Sosulski and Korc, 2011). According to many authors (Lenart et al., 2005; Piechota, 2005; Gong et al., 2009) regular use of manure, or the combined use of organic and mineral fertilization, increases organic matter content in soils, and may have positive influence on the soil quality.

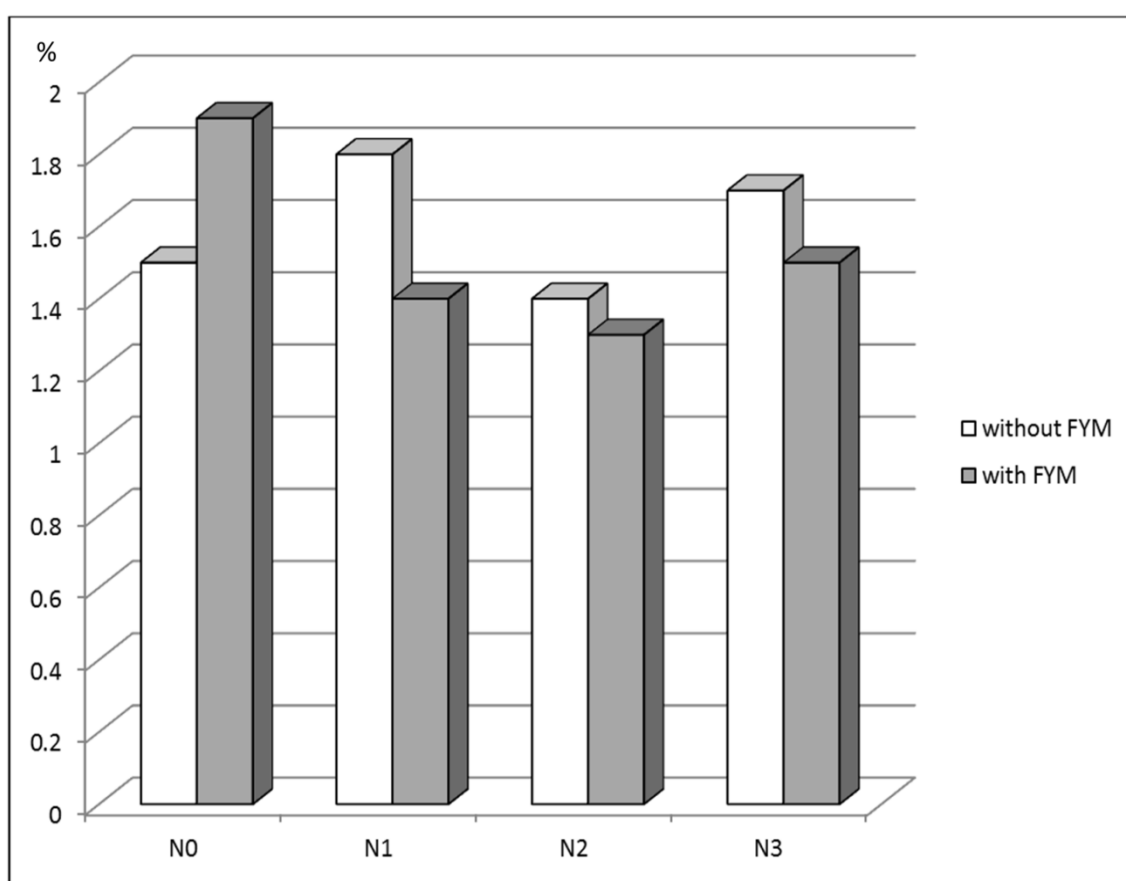
The consequence of changes in the content of organic carbon and total nitrogen, are changes in the ratio of TOC/TN. It is generally known that the FYM application results the reducing of this ratio value, due to increased concentration of nitrogen than carbon. It has been calculated that the TOC/TN ratio under the influence of investigated fertilization ranged from 9.4 to 12.8 (Table 2). The highest values of this ratio were found after N_2 dose ($93.3 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$). It was also noted that the use of manure and different nitrogen doses resulted in a slight decrease in the ratio of TOC/TN, which certainly did not cause the intensity of mineralization in soil (Mando et al., 2005).

Changes in the content of total organic carbon in soil, as a result of fertilization (particularly manure application), are leading to changes in the content of dissolved organic matter - DOM (Schulz et al., 2002). It is the most mobile fraction consisting mainly of low-molecular-weight organic compounds, including low-molecular fraction of humic substances. The mobility of dissolved organic carbon in the soil is a crucial factor in the transport of carbon in the ecosystem and the formation of organic matter (Neff and Asner, 2001).

In the present study soluble organic matter was determined as dissolved organic carbon (DOC), which depends primarily on the type of deposited/delivered organic material to soil and microbial activity (Marinari et al., 2010). The content of the DOC before the foundation of the experiment was $234.04 \text{ mg}\cdot\text{kg}^{-1}$. However, after 36 years of application of different nitrogen doses without FYM, DOC ranged from 122.4 to $152.2 \text{ mg}\cdot\text{kg}^{-1}$ (Table 2). The application of same nitrogen doses simultaneously with FYM increased the DOC content, which ranged from 133.5 to $166.7 \text{ mg}\cdot\text{kg}^{-1}$. The value of this parameter was significantly determined only by the 2nd factor, application of nitrogen and manure, and it was 10.7% higher in comparison with 1st factor – different doses of nitrogen. According to the literature (Neff and Asner, 2001; Dębska and Gonet, 2002; Nardi et al., 2004; Sosulski et al., 2013), the content of dissolved carbon in agricultural soils varies depending on the method of fertilization and species of cultivated plants, which was also confirmed in the present studies. It should be noted that changes in the DOC content did not affect the percentage of this fraction in the total organic carbon (TOC) (Table 2, Figure 3). Percentage of DOC in total organic carbon content (TOC) was 1.6% on average, and before the

foundation of the experiment was 1.8%. Low share of this carbon fraction may indicate that it depends directly on the absolute amount of organic matter or is also related to the type of soil (Gonet and Dębska, 2006). There was no significant influence of applied nitrogen fertilization with and without manure, on the percentage of this carbon fraction in the total organic carbon content in analyzed soil.

The essential information about, the characteristics of humic substances in the soil provides a ratio of absorbance at two wavelengths of 465 and 665 nm. This ratio is widely used to characterize humic substances (Jing-an et al., 2007; Kondratowicz-Maciejewska et al., 2011). With the increase of molecular weight and the degree of condensation of aromatic rings of humic acids (HA), the ratio $A_{4/6}$ decreases (Senesi et al., 2003; Kalembasa and Becher, 2009).



N₀-N₃ – nitrogen doses, □ – without FYM application, ■ – FYM application

N₀-N₃ – dawki azotu, □ – bez nawożenia obornikiem, ■ – nawożenie obornikiem

Figure 3. The percentage of dissolved organic carbon (DOC) fraction [%] in total organic carbon (TOC) content

Rysunek 3. Procentowa zawartość frakcji rozpuszczonego węgla organicznego (RWO) [%] w zawartości ogólnego węgla organicznego (OWO)

After the application of different nitrogen doses, humic acids of analyzed soils were characterized by lower value (5.4 on average) of $A_{4/6}$ indicator in comparison to the

value of this indicator after application of nitrogen doses with manure - 6.3 (Table 2). Farmyard manure application can cause the formation of humic acids of lower molecular weight and a low humification degree. This indicates the higher content of humus in the early stages of its formation and aliphatic structure of humic acids (Kondratowicz-Maciejewska, 2009; Xiang-yun et al., 2014).

Conclusions

After 36 years of using different nitrogen doses together with farmyard manure and the cultivation of plants in a simplified crop rotation (potato-rye-rye) it was found that TOC, TN, DOC in a sandy loam soil were higher compared to the values of these parameters determined only after mineral nitrogen fertilizers application. Long-term application of mineral nitrogen (46.7 , 93.3 and $140 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$) with manure ($30 \text{ t}\cdot\text{ha}^{-1}$), which is the source of organic matter in soil in the early transformation stages of humus, resulted in an increase in the value of the absorption ratio ($A_{4/6}$). This indicates an increased content of low-molecular-weight humic substances. These compounds are a fraction of labile organic matter and therefore more available to the plant, which was confirmed by the content of DOC (156.9 - $166.7 \text{ mg}\cdot\text{kg}^{-1}$). Thus, no negative long-term effect can be concluded with respect to different doses of nitrogen fertilizer and manure on the quality of sandy loam soil in terms of the characteristics of organic matter.

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