

FUNCTION OF A SHELTERBELT AS A BIOGEOCHEMICAL BARRIER
IN THE AGRICULTURAL LANDSCAPE*

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A b s t r a c t. The function of a shelterbelt as a biogeochemical barrier located on two different kinds of soil: mineral and mineral-organic, was investigated on the background of changes in the total nitrogen content, average yearly concentration of ammonia, nitrate ions, activity of urease, and structure of humic acids. Transformation of different nitrogen forms in the soil under the shelterbelt was strongly connected with the humification processes and molecular structure of humic acids.

K e y w o r d s: shelterbelt, mineral and organic forms of nitrogen, activity of urease, humic acids, E_{4/6}, EPR, thermal analysis

INTRODUCTION

Nitrate pollution caused by the use nitrogen fertilizers is an especially serious threat for the rural areas. Many physical, chemical and biological processes control dispersion of nitrates in soils. In all these processes, nitrogen undergoes a wide variety of transformations, most of which involve organic matter, in particularly humic substances. So far, investigations on humic substances and their transformation in soils under shelterbelt have not been done.

In the agricultural landscape with a high-level of fertilization in the cultivated fields, elements of the landscape which can protect water bodies against eutrophication, are of particular importance. This protective function is partly performed

*This work was supported by a grant No.6 PO6S 004 21 founded by KBN.

by meadows and forest ecosystems. It was shown that shelterbelts (mid-field rows of trees afforestation) and stretches of meadow to help in the collecting of water-borne movement of various chemical compounds from the cultivated fields into the collecting water basin [9]. One of the methods of controlling substance circulation in the agricultural landscape is to create a biochemical barrier [2,3,7].

The goal of this study was to investigate the influence of shelterbelts in the agricultural landscape on the transformation of inorganic and organic forms of nitrogen in the soil, as well as on the chemical structure of humic acids (HA) in order to understand their role in the functioning of shelterbelts as biogeochemical barriers.

MATERIALS AND METHODS

The investigations were carried out in the soils under shelterbelt with a total length of 125 m located in the Agroecological Landscape Park in Turew (40 kilometers south of Poznań, West Polish Lowland). The location of this shelterbelt is 16° 45 E and 52° 01 N. One part of this shelterbelt is located on mineral soils and the other on the mineral-organic soil. According to the Polish Systematics [5], soils were classified into the following units: division, order, type and subtype (Table 1). Deciduous afforestation included various species of trees with the predominance maple, ash, beech and hawthorn. In the underground, elder, lilac, a companion crop of maple, ash and hawthorn dominated. Samples were taken from five chosen sites marked as Nos 1-5 each month in 2000 from a depth of 0-20 cm. After five individual samples had been taken, they were mixed to give the so-called an average mixed sample. Then roots and stones were removed. When air-dry state was reached, aggregated mineral particles were ground and sieved through a sieve with 1 mm diameter.

The content of organic carbon in the mineral soils ranged from 2.2 to 2.7%. Mineral-organic soils were characterized by a higher content of organic carbon 3.2-3.9%. Total nitrogen in the soils was estimated by Kjeldahl method, ammonium and nitrate ions by Spurway method, and activity of urease by Hoffman and Teicher technique [14].

Humic acids (HA) from the soil samples were collected during a seven month (period from April to October) and extracted with 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$ at pH 7.00 ± 0.01 under nitrogen atmosphere [15]. According to the sites of sampling marked as Nos 1-5, HA from the mineral soils were marked as HA1, HA2, HA3, and those from the mineral-organic soils as HA4 and HA5.

Table 1. Content of N-total (mg/100g of soil), N-NO₃ (mg N/100g of soil), urease activity (g urea hydrolyzed·g⁻¹soil·h⁻¹), N-NH₄ (mg N/100g of soil) and pH in the mineral (1-3) and mineral-organic soils (4-5) in 2000

Soils	Analysis	Dates									
		8.III	11.IV	8.V	6.VI	9.VII	7.VIII	5.IX	10.X	12.XI	Mean
1	N-Total	208.9	166.9	178.6	140.6	145.6	129.4	181.4	136.6	161.3	159.0
	N-NO ₃ ⁻	2.8	1.4	2.0	1.4	1.7	1.0	1.7	1.4	1.0	1.6
	Urease activity	7.3	9.7	13.0	5.3	7.9	3.9	9.1	8.1	9.6	8.2
	N-NH ₄ ⁺	2.4	2.2	1.6	1.7	2.6	2.2	2.3	1.0	1.9	2.0
	pH	5.2	4.3	5.8	4.5	4.8	5.3	5.2	5.2	5.3	5.1
	N-total	179.3	195.4	153.4	110.3	140.6	94.6	174.2	175.8	108.3	147.0
2	N-NO ₃ ⁻	1.8	1.0	1.2	0.7	1.0	0.7	1.3	0.7	1.3	1.1
	Urease activity	8.8	10.6	2.9	5.8	5.9	3.3	6.7	5.7	6.1	6.2
	N-NH ₄ ⁺	1.1	1.9	0.6	1.2	1.9	1.0	2.0	0.5	1.2	1.3
	pH	4.2	4.3	3.9	4.4	4.0	4.1	4.0	4.2	4.1	4.1
	N-total	135.5	128.6	76.7	71.7	101.4	106.1	148.4	110.3	138.9	113.0
	N-NO ₃ ⁻	1.6	1.1	1.1	0.8	0.7	0.9	0.5	0.4	0.7	0.9
3	Urease activity	5.9	9.1	5.8	2.4	6.9	3.1	6.6	4.5	5.1	5.5
	N-NH ₄ ⁺	1.2	1.4	0.5	0.6	1.4	1.2	1.3	0.3	0.9	1.0
	pH	4.5	4.2	4.0	3.9	4.1	4.0	4.1	3.9	4.0	4.1
	N-total	268.2	205.0	242.5	168.0	135.5	235.8	182.6	234.1	221.8	210.4
	N-NO ₃ ⁻	1.2	0.4	1.6	1.0	1.2	0.9	0.7	0.8	0.7	0.9
	4	Urease activity	39.4	29.2	42.7	46.2	17.0	61.6	36.9	34.9	44.2
N-NH ₄ ⁺		1.5	1.0	1.1	0.8	0.8	1.0	1.3	1.0	1.0	1.1
pH		7.3	6.9	7.2	7.1	7.1	7.3	7.2	7.1	7.3	7.2
N-total		314.7	249.8	332.6	197.7	263.2	329.3	280.6	290.1	252.0	278.9
N-NO ₃ ⁻		1.9	0.8	2.5	1.6	1.9	2.5	0.9	1.0	0.9	1.6
5		Urease activity	45.5	64.7	67.3	70.3	58.6	79.8	57.1	60.7	59.7
	N-NH ₄ ⁺	2.5	1.3	1.4	1.1	1.0	3.1	2.1	1.8	2.2	1.8
	pH	7.5	7.0	7.3	7.2	7.2	7.3	7.1	6.9	7.4	7.2

Where: 1. Division-autogenic soils, order-brown forest soils, type-hapludalfs, subtype-glossudalfs. 2. Division autogenic soils, order-brown forest soils, type-hapludalfs, subtype-glossudalfs. 3. Division-autogenic soils, order-brown forest soils, type-hapludalfs, subtype-ochraquals. 4. Division-hydrogenic soils, order-post-bog soils, type-mucky, subtype-muckous. 5. Division-hydrogenic soils, order-post-bog soils, type-mucky soils, subtype-muckous.

The chemical structure of the HA was investigated by the VIS spectroscopy, EPR technique, and thermal analysis. Optical densities of 0.01% HA (w/v) solutions in 0.1 M NaOH were measured at 465 nm (E_{465}) and 665 nm (E_{665}) on a spectrophotometer DU 68 (Beckman, USA) and used to calculate E_4/E_6 ratios. EPR spectra were recorded using a modified X-band spectrometer RE-1301 (Russia) at room temperature under air atmosphere.

Thermal properties of the HA were investigated in a nitrogen atmosphere using a OD-103 derivatograph (MOM, Hungary) at a heating rate of 10 deg/min up to 1000° C with Al_2O_3 as a reference substance. The curves of differential thermal analysis (DTA), thermogravimetry (TG), and differential thermogravimetry (DTG) were recorded simultaneously. Weight losses in different temperature regions were calculated from TG curves.

All the experiments were run in triplicate and the results averaged.

RESULTS AND DISCUSSION

In all soil samples analyzed, regardless of the sampling period, the amount of total nitrogen, urease activity, concentration of ammonium and nitrates were much higher in the mineral-organic soils than in the mineral soils (Table 1). Mineral-organic soils belong to hydrogenic soils in which organic matter content ranged from 5.5 to 6.7%. Mineral soils belong to autogenic soils in which organic matter content is lower and ranges from 3.8 to 4.7% [14]. It was found that in all the sampling periods, along with an increase in the distance from the edge of afforestation localized in the mineral soil, there was a decrease in the amount of total nitrogen from 13.8 to 49% (Table 1). The lowest decrease was observed on the 12th of November and the highest on the 8th of May.

In the mineral-organic soils, higher contents of total of nitrogen were found than in the mineral soils (135.5-329.3 mg/100 g of soil). Unlike the mineral soils, in mineral-organic soils, an increase in total nitrogen content was observed with an increase in the distance from the edge of the shelterbelt. The highest increase was observed in July, August and September and ranged from 34.9 to 45.8%, and the lowest in the spring during April to July from 15 to 27.1%.

A similar direction of changes was observed in content of nitrate ions (Table 1). In the mineral soils, an increase in the distance from the edge of the shelterbelt was accompanied by a decrease in the concentration of nitrates, with the highest decreases observed in September and October (from 70.6 to 71.4%), and the lowest between April and June (from 21.4 to 42.8%). In the mineralorganic soils, an

increase in the content of this ion with an increase in the distance from the edge of the shelterbelt ranged from 20 to 64%.

As in the case of total nitrogen, similar changes were observed in the activity of urease (Table 1). This enzyme participates in the hydrolytic decomposition of urea. Ammonia produced during this process is strongly adsorbed by the soil, which makes it safer in the case of larger nitrogen losses, easily accessible to plants. In the mineral soils, urease activity decreased with an increase in the distance from the edge of the shelterbelt, with the lowest on the 9th of July (13.2%), and the highest on the 8th of May and 6th of June (53.4-54.7%), (Table 1). The changes observed can be explained by trees that stimulate changes in the sorptive complex and effectively restrain migration of various substances from the soil solution. Soil ability to stop the process of decomposition and retention of chemical bonds depends on its own attributes, including clay fraction, organic substances, reaction base, exchange capacity [12].

While analyzing changes in the urease activity in the investigated samples of both soils, it was confirmed that similar changes took place for nitrogen. It was shown that the activity of urease in the mineral soils was the highest in May, September, and November, and in the mineral-organic soils in August. As it is well known, urease is one of the indicators of soil biological activity related to the soil type. Seasonal changes in this activity depend mainly on moisture, temperature and microflora. In the study year, exceptionally intensive rainfalls were observed in July (148 mm) and in August (154 mm). In those months, air temperature was also the highest (in July 19.8^o C) and in August 21.8^o C). This drastic increase in the amount of rainfall and temperature was accompanied by an increase in the activity of urease in that period ranging from about 3.9 to 9.1 g urea hydrolyzed g⁻¹ soil h⁻¹ in the mineral soil. In the second soil, the activity of this enzyme was the highest in July, i.e., 79.8 g urea hydrolyzed g⁻¹ soil h⁻¹. Similarly, urease activity together with nitrogen mineralization during the vegetation season was strongly related to soil temperature and moisture. This type of increase in the concentration of total nitrogen and urease activity during summer period was most likely caused by the activity of soil microbes producing an increase in urease with a temperature increase (Table 1).

Chemical composition of organic matter in the mineral-organic soils and their sorbing characteristics make them rich in nitrogen and organic compounds, mainly amino acids. Mineralization processes and differentiation in the water movement cause changes in the chemical composition, mainly nitrogen forms in these soils. Also microbiological activity in the soil is responsible for the changes in the

chemical composition of organic matter, as a function of agroecological, physical and chemical quality of these soils and in particular the quality of organic matter [13]. Studies showed that urease activity responsible for changes in the nitrogen organic compounds were from 21 to 71 times higher in the mineral-organic soils as compared to the mineral soils (Table 1).

Considerable differences were shown in the pH values of both kinds of soils. pH of the mineral soils indicated that these soils were very acidic and acidic, while the mineral-organic soils were neutral (Table 1). An increased enzyme activity resulted in an increased ammonia and urea production. A higher content of ammonia is most likely caused by an increase in the pH level in that period. Relations between pH levels were also analyzed for that period. (Table 1).

In the mineral soils, the content of ammonium during entire vegetation season decreased along with an increase in the distance from the edge of the shelterbelt. The highest decrease was observed from May to June and ranged from 64.7 to 68.8 mg N/100 g of soil. In the same time period, higher activity of urease observed mean that urease participates in the formation of ammonium in the soils under the shelterbelt.

Comparing pH changes in both analyzed soils, it can be stated that the sorptive complex in the mineral soils reacted differently than in the organic soils to the increase in the rainfall rate and temperature. In the mineral soils, more time was needed to buffer ions than in the organic soils. The result of this phenomenon was probably, differentiation of the sorptive complex in the structure of these soils. Contrary to the mineral soils, the sorptive complex of the mineral-organic soils tested contains more organic bonds with the following free groups: -COOH, -OH, -NH₂, =NH, -SH. These groups are strong organic ion exchangers. They are more capable of complexing chemical compounds than the sorptive complex of the mineral soils [11,13].

There are significant differences between the parameters of the VIS spectra of HA from the two kinds of soils (Table 2). HA from the mineral-organic soils are characterized by a significantly higher optical densities at 465 nm and lower E₄/E₆ ratios compared to HA from the mineral soils. This reflects a higher degree of condensation and polyconjugation in the molecules of HA from the mineral-organic soils compared to those from the mineral soils [4,6,10]. A decrease in E₄₆₅ with an increase in the distance from the edge of the shelterbelt for HA from both soils can be seen. It indicates a decrease in the degree of polyconjugation in their molecules in this direction.

EPR spectra of HA consist of a narrow-line signal with g value 2.0033-2.0036 (Table 2). According to the conception accepted by the present authors, this signal

Table 2. Parameters of VIS and EPR spectra of HA

Sample	E ₄₆₅	E ₆₆₅	E ₄ /E ₆	Width of EPR signal ΔH , gs	g-value	Intensity of EPR signal $I \cdot 10^{17}$ spin g ⁻¹
HA1	0.330	0.052	6.35	4.9	2.0035	5.28
HA2	0.287	0.043	6.67	6.5	2.0035	2.21
HA3	0.255	0.050	5.10	6.2	2.0036	1.80
HA4	0.470	0.088	5.34	6.2	2.0033	5.86
HA5	0.405	0.073	5.55	6.2	2.0035	3.74

results from paramagnetic centers (PMC) of the aromatic polyconjugation systems in the HA molecules. The parameters of this signal (width H, g-value, intensity I) reflect, to a considerable degree, dimensions and structure of the aromatic polyconjugation systems in HA [1].

For the mineral soil, an increase in the distance from the edge of the shelterbelt leads to a decrease in the intensity of the organic PMC signal in the EPR spectra of HA, indicating a decrease in the dimensions of the aromatic polyconjugation systems in their molecules. Transition from mineral to mineral-organic soil is accompanied by a considerable rise of the organic PMC signal intensity, which reflects a more extended system of polyconjugation in the HA from the mineral-organic soil than from the mineral soil. A further increase in the distance from the edge of the shelterbelt leads to a decrease in the intensity of the EPR signal. These data are in compatible with the results of VIS spectroscopy (Table 2).

Table 3 shows weight losses of HA samples in the various temperature zones. In the zone of up to 300°C thermochemical reactions of a thermolable part of HA molecules undergo mainly dehydration and decarboxylation [8]. Thermal decomposition of a more thermostable skeleton part of HA takes place from 300 to 500°C. As a result of the breaking off aliphatic bridges between aromatic structural units, aromatic compounds are eliminated with the highest rate. For the temperature zone from 500 to 800°C, the second reactions of charcoal formation and destruction of especially thermostable aromatic and heterocyclic fragments of HA molecules are suggested [8]. Parameter Z reflects a ratio between thermolable and thermostable parts of the humic molecules.

For HA from both kinds of soils, weight losses in the temperature region of up to 300 °C as well as parameter Z increase with an increase in the distance from the edge of the shelterbelt (Table 3). This indicates an increase in the content of thermolable structural units (carbohydrates, free and bound functional groups) and a

Table 3. Data of thermogravimetric analysis of HA

Sample	Weight losses in temperature regions, % on organic matter, °C							$Z = \frac{\text{up to 300}}{300 - 500}$
	up to 200	200-300	up to 300	300-400	400-500	300-500	500-800	
HA1	7.57	15.90	23.47	11.35	9.04	20.39	21.24	1.15
HA2	10.75	19.20	29.95	13.06	9.99	23.05	23.80	1.30
HA3	13.28	16.98	30.26	11.91	8.85	20.66	21.40	1.46
HA4	8.73	16.72	25.45	16.00	9.46	25.46	24.73	1.00
HA5	13.23	18.64	31.87	13.23	9.62	22.85	20.45	1.40

decrease in the thermostable skeleton part of HA molecules with an increase in the distance from the edge of the shelterbelt.

Therefore, the molecular structure of HA from the soils under the shelterbelt depends on the kind of soil and distance from the edge of the shelterbelt. HA from the mineral-organic soil are characterized by a higher degree of condensation and a more extended systems of aromatic polyconjugation compared to HA from the mineral soils. This difference is caused by different conditions for humification process in these soils. A neutral medium and a considerable content of organic and inorganic forms of nitrogen in mineral-organic soil compared with the mineral soil (Table 1) are favorable for the humification process producing HA with a higher degree of humification, or chemical maturity [6].

For both kinds of soils, an increase in the distance from the edge of the shelterbelt is accompanied by similar trends in the changing of the molecular structure of HA: a rise in the content of carbohydrates, carbonyl containing groups and other thermostable functionalities, as well as a reduction of the content of the thermostable skeleton part of molecules and a degree of aromatic polyconjugation which reflects the lowering of a degree of humification, or chemical maturity of HA in this direction. For the mineral soil, this fact may be connected with a decrease in the inorganic and organic forms of nitrogen, as well as biological activity in the same direction.

The highest contents of total nitrogen, nitrate and ammonium ions in the soil sample No. 1 taken at the beginning of the shelterbelt are caused probably by an input of additional inorganic nitrogen compounds from the adjoining cultivated field. It is known that assimilation of inorganic forms of nitrogen in the microbial biomass through immobilization process leads to the transformation of inorganic nitrogen into organic forms with subsequent incorporation into humic substances [12]. Abiotic reactions between inorganic nitrogen and organic matter also play a role. Through these processes, an additional content of inorganic nitrogen and a high level of biochemical activity in the soil No1 may lead to the formation of HA

with the highest degree of humification (Tables 2 and 3). With an increase in the distance from the edge of the shelterbelt, the content of inorganic and organic forms of nitrogen, as well as biochemical activity of the soil decrease. This, in turn is the cause of a decrease of humification degree, or chemical maturity of HA. Therefore, transformation of various nitrogen forms in the soil under the shelterbelt is strongly connected with humification process and molecular structure of HA.

Hence, the function of the shelterbelt as a biogeochemical barrier reducing nitrate pollution of ground water in the agricultural landscape is strongly connected with humification process leading to the transformation of extra inorganic nitrogen into stable organic forms in the humic substances.

On the other hand, for the mineral-organic soil, the content of total nitrogen and its inorganic forms, as well as urease activity increase with an increase in the distance from the edge of the shelterbelt while the degree of humification of HA considerably decreases. This phenomenon can be due not only to the influence of the shelterbelt but also to other effects, one of which may be different conditions of humification in the sites located at a different distance from the pond (different water regime).

CONCLUSIONS

1. The present investigation has shown the impact of the kind of the soil and distance from the edge of the shelterbelt on changes of the total nitrogen content, average yearly concentration of ammonium and nitrate ions, urease activity, and the chemical structure of HA.

2. The shelterbelt located on the mineral soil decreases inorganic nitrogen compounds in the soil with an increase of distance from the edge of the shelterbelt.

3. Humic acids from the mineral-organic soil under the shelterbelt are characterized by a higher degree of condensation and aromatic polycondensation compared to those from the mineral soils. For both kinds of soils, an increase in the distance from the edge of the shelterbelt is accompanied by a decrease in the degree of humification, or chemical maturity of HA.

4. The function of the shelterbelt as a biogeochemical barrier reducing nitrate pollution of ground water in the agricultural landscape is strongly connected with humification process leading to transformation of an extra inorganic nitrogen into stable organic forms in humic substances.

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FUNKCJA ZADRZEWIENIA JAKO BARIERY BIOGEOCHEMICZNEJ
W KRAJOBRAZIE ROLNICZYM

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S t r e s z c z e n i e. Przedstawiono funkcjonowanie pasa zadrzewień jako bariery biogeochemicznej zlokalizowanej na dwóch typach gleb: mineralnej i mineralno-organicznej na podstawie zmian azotu ogólnego, średniego rocznego stężenia jonów amonowych, jonów azotanowych, aktywności ureazy, pH oraz badań struktury kwasów huminowych (HA). Stwierdzono zależność transformacji różnych form azotu w glebie pod pasem zadrzewień od procesu humifikacji oraz molekularnej struktury HA.

S ł o w a k l u c z o w e: pas zadrzewień, formy azotu, aktywność ureazy, kwasy huminowe, krajobraz rolniczy