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Original Research

The Role of Black Locust (*Robinia pseudoacacia* L.) Shelterbelts in the Stabilization of Carbon Pools and Humic Substances in Chernozem

Ryszard Mazurek[1]*, Romualda Bejger[2]

[1]Department of Soil Science and Soil Protection, University of Agriculture in Kraków,
Al. Mickiewicza 21, 31-120 Kraków, Poland
[2]Department of Physics and Agrophysics, West Pomeranian University of Technology, Szczecin,
Papieża Pawła VI nr 3, 71-459 Szczecin, Poland

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Abstract

The purpose of our study was to evaluate the spatial arrangement of carbon pools and humic substances maturity in cultivated chernozem soil adjacent to black locust shelterbelt. A plot on arable land adjacent to mid-field shelterbelts in southern Poland (Proszowice Plateau) was chosen. Soil samples were taken at different distances from the shelterbelt from a depth of 0-25 cm. Samples were also collected from under the shelterbelt. The pools of organic carbon were highest in samples taken from the farmland closest to the black locust trees. As distance from trees increased, content of humic substances and fulvic acids was found in cultivated soil to be significantly lower. Based on the van Krevelen diagram, it can be concluded that the most mature and the most stabilized humic acids are those in the soil located directly adjacent to the trees.

Keywords: organic carbon pools, humic acids, land use, loess soil

Introduction

In Europe, *Robinia pseudoacacia* is regarded as a species of foreign origin. Its primary region of occurrence was North America. At first, it was cultivated in Europe as a park and garden tree. Today it is grown in parks but it also grows in forests (Hungary, Slovakia). Black locust trees were planted in Poland mainly for erosion control. For example, it was grown to strengthen ravine walls in the loess highlands in southern Poland and as protection against wind erosion in the Wielkopolska Lowland [1].

Robinia pseudoacacia is characterized by poor soil requirements. It is very resistant to drought, spring frosts, and salinity. It requires full light and is best grown in loose and permeable soils, but not clayey and wet soils. Due to modest edaphic requirements, black locust is used for reforestation of all wastelands, especially with dry, poor soil [2]. Planting black locust is often done to help reclaim former quarries and areas damaged by human activity [3].

Black locust lives in symbiosis with root bacteria of the genus *Rhizobium*. The ability of the black locust to improve the content of nitrogen and carbon in forest soils has been reported previously [4].

Black locust planted in agroforestry systems can improve soil C status in an agroecosystem through storage of CO_2 in the biomass of woody plants. A consequence of the presence of black locust trees is an increased accumulation of carbon as soil humus [5]. *Robinia pseudoacacia* used in agroforestry systems, or present in shelterbelts, may contribute to the carbon content in soils. The incorporation of the easily decayed leaves and flowers is the main contribution, which is facilitated by a narrow C/N ratio. In addi-

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*e-mail: rrmazure@cyf-kr.edu.pl

tion, tree roots may be destroyed as a result of mechanical tillage, and then decomposed. There is an additional supply of organic matter in the arable soils located in the ecotone zones – in the vicinity of the shelterbelts. In both farmland soil and forest soil, a large amount of tree-derived organic material can be found on the soil surface or in the soil. In this area, the so-called "marginal effect" can be observed [4, 6].

Additional input of aboveground (leaves, flowers, fruits, twigs) and underground (rhizodeposits) tree debris can lead to the sequestration of C in soil. Carbon sequestration is mainly associated with selective preservation of recalcitrant compounds and recalcitrant humic substances (HS). There is division of resistance of organic matter compounds against microbial decomposition on the primary recalcitrance (plant litter and rhizodeposits) and the secondary recalcitrance of microbial products (humic polymers and charred materials) [7].

The process of selective preservation leads to the accumulation of recalcitrant molecules. Alkyls and aromatics are examples of the most recalcitrant compounds of soil organic matter. Humic substances in soil are biochemically stabilized due to the soil's chemical composition and complexing processes. Lignin and polyphenols are stabilized compounds of HS [8].

Environmental and biological factors, e.g. dominant pedological processes, land use type, and fertilization play an important role in stabilizing the chemical structure of humus. For example, humic acids (HAs) from the agricultural use of chernozem are characterized by a higher degree of humification. This means that HAs in chernozem are more stable compared to other soils [9].

Stabilization of soil organic carbon (SOC) and resistance against microbial decomposition may be indirectly considered due to the content of most of the humified compounds in HS as well as due to the aromaticity and condensation of HAs. The maturity and stability of HS can be measured based on chemical and spectrophotometric methods [8]. Such parameters are connected with the chemical composition of HAs (e.g. atomic ratios H/C, ω), as reflected on their spectral parameters (e.g. $E_{2/4}$, $E_{4/6}$, $\Delta\log K$).

Changes in the composition of HS and HAs due to the effect of the shelterbelts may have repercussions on the general state of soil fertility and may be reflected in crop yields [10]. For this reason, it is necessary to compare the stability and chemical composition of humus in the soil cultivated in the vicinity of shelterbelts (including the area composed of black locust trees), and in the soil located farther from the trees. Such a comparison can prove helpful in the eventual promotion of the beneficial effects of shelterbelts on treeless areas, i.e. the loess soils of southern Poland.

The aim of this study was to provide a detailed characterization of carbon pools, and a detailed characterization of the stability of HS and HAs against microbial decomposition in arable loess soils on the Proszowice Plateau. The degree of humification, maturity, and other parameters were measured. The distance of black locust trees to the studied arable loess soil of the Proszowice Plateau was another factor that was taken into account. The benefits and negative aspects of black locust shelterbelts on soil fertility were also evaluated. Such an evaluation is important for agricultural practices.

Our working hypothesis was that carbon pools and HS will differentiate in proportion to the distance from the black locust trees. We expected that since black locust is a nitrogen fixing tree (NFT), it can improve HA maturity, stabilization, and resistance against microbiological decomposition.

Material and Methods

An arable field in the Proszowice Plateau (southern Poland) was selected for soil sampling. The Proszowice Plateau is located in a temperate climatic zone with an average precipitation of 550 mm, and a mean yearly temperature of 7.7ºC. The investigated field was located in the village of Dolany located at 50º 8' 24.88" N, 20º 28' 32.84" E. The field chosen was flat, so as to exclude the possible effects of soil slides and surface runoff, on the soil properties. In the chosen location, cereals and tobacco were mainly cultivated. Spring wheat was cultivated the year before the sampling was done. The fertilization dose expressed in pure element of NPK ratio amounted to 130:60:90.

The field was in the immediate vicinity of the midfield shelterbelt. The only trees on the shelterbelt were black locust trees (Fig. 1). The black locust trees were 50 years

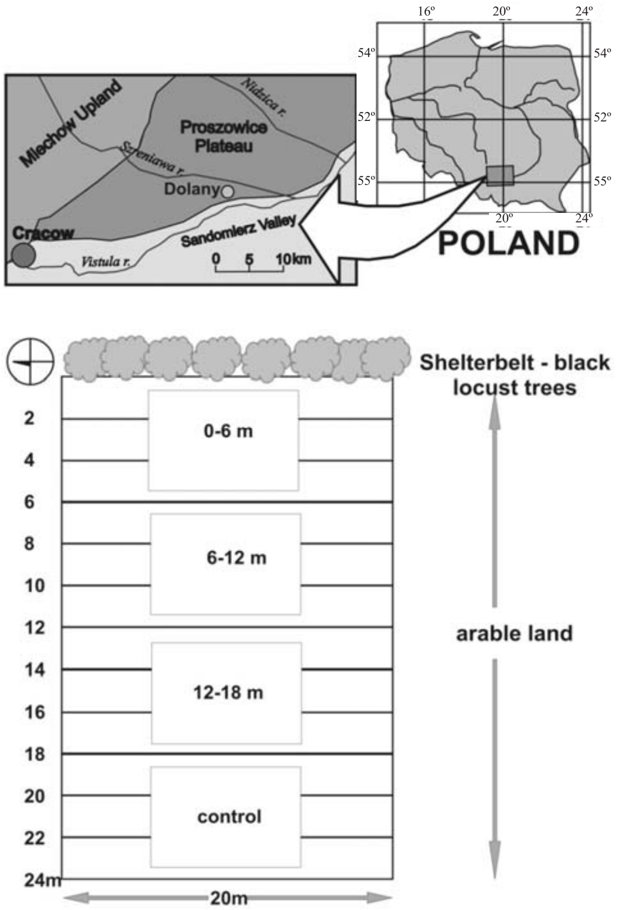

Fig. 1. Location of the investigated area, and soil sampling design.

Table 1. Chosen soil properties of representative profile.

Horizon	Depth cm	pH		Diameter fraction in mm			SOC	Nt	SOC/Nt
		H_2O	KCl	2-0.05	0.05-0.002	<0.002	$g \cdot kg^{-1}$		
Ap	0-33	6.29	5.25	15	74	11	13.06	1.50	8.72
A2	33-47	6.54	5.37	15	60	15	10.39	1.39	7.56
ABw	47-76	6.73	5.41	18	62	20	4.39	1.21	3.63
C	76-149	6.94	5.62	18	60	12	2.78	0.91	3.05

old. Shelterbelts were originally planted on the borders of fields to protect the loess soil against water and wind erosion. An arable field had been cultivated where the shelterbelts now reside. Shelterbelts of black locust were planted on loess areas as midfield shelterbelts in the XX century. The shelterbelts were meant to be one of the phytomellioration factors used to decrease loess soil erosion.

The studied shelterbelt was narrow, with a width of 2-3 m. Tree height was 10-12 m. The diameter (DBH) of the trees was 30-40 cm. The crown span of trees was 6-8 m and the distance between trees was 2-4 m.

A selected representative soil profile was performed on the plot. The soil type and subtype were determined according to the current Polish classification and WRB [11, 12]. Soil material from each horizon was sampled to find out the basic properties. Soil pH was measured potentiometrically. Soil fraction content was measured according to the Casagrande method. The content of organic carbon was determined using a Leco CNS 2000 analyzer.

The field was separated into a 20×24 m plot, and then divided into 12 rectangular areas (subzones) of 2×20 m. Subzones were then divided into 5 rectangular microplots (2×4 m) (Fig. 1). The overall number of samples was 60 (12 subzones X 5 microplots). In spring 2008, 60 samples from a depth of 0-25 cm were collected from each microplot with an Egner stick to determinate the carbon pools. In the same time period, undisturbed soil cores were sampled to investigate bulk density. Next, part of the soil material from each of the 12 subzones were mixed to investigate the composition of humic substances in detail. The determined results were aggregated into 4 groups (zones) according to their distance to the trees: 0-6 m, 6-12 m and 12-18 m, and the control (18-24 m). In spring 2008, soil samples from under the shelterbelt were also taken.

According to the literature, this method of sampling showed that soil properties in the vicinity of the trees are most diverse at a distance equal to the height of the trees. The strongest ecological interaction zone of trees and crops shall be equal to the distance from the tree and one to two times the height of the trees [13].

Table 1 presents the basic characteristics for the systematic determination of the representative profile. The soil was classified to the chernozem with cambic epipedon type based on the Polish classification [12]. The soil was also classified according to the principles of WRB [11], as Haplic Phaeozems (Siltic). Soil was characterized by a silt loam soil texture. Chernozem reaction was slightly acidic in the A horizon.

In the collected soil the following materials were determined:

a) Soil organic carbon (SOC) content. The SOC content was determined according to the spectrophotometric method of Orlov and Grindel [14]. The absorbance of the soil solutions was measured at λ=590 nm using a computer-controlled spectrophotometer SPECORD UV-VIS M-42 (Carl Zeiss Jena).

b) The soil organic carbon pools. The organic carbon pools in the different soils were better characterized than the SOC content [15]. The soil organic carbon pools were calculated in the 0-25 cm layer based on the organic carbon content (SOC) and bulk density. SOC pools were calculated according to equation [2]:

$$SOC\ pools = SOC \times BD \times 0.25 \times (1 - \frac{Si}{100}) \times 10{,}000 \quad (1)$$

...where BD means bulk density and Si content of coarse fraction >2 mm. The annual rate of SOC pools was calculated as the difference between those SOC pools determined in particular zones and those SOC pools determined in the control, divided by the age of the trees.

c) Distribution of carbon in the main fractions of humic substances (HS). The content of HS was determined using the method proposed by the International Humic Substances Society. Distribution of carbon in the main fractions of HS in the humic (C_{HA}) and fulvic acids (C_{FA}), and the C_{HA}/C_{FA} ratio was calculated [15].

d) The elemental composition (C, H, N, O) in HAs. This composition was determined using the analyzer CHNS/O Vario EL II (Elementar Analysensysteme GmBH). The elemental composition was determined in HA samples dried at 105ºC. The chemical composition was calculated based on atomic ratios H/C, O/C, O/H, and internal oxidation degree (ω) according to equation [16]:

$$\omega = \frac{(2O + 3N) - H}{C} \quad (2)$$

e) Spectral ratios of HAs. Determination of $E_{2/4}$ (as absorbance ratio at 280 nm and 465 nm), $E_{4/6}$ (as

Table 2. Soil organic carbon pools, soil organic carbon content (SOC), yield of humic substances (C_{SH}), humic acids (C_{HA}), fulvic acids (C_{FA}), and C_{HA}/C_{FA} ratio.

Distance from trees [m]	SOC pools Mg·ha^{-1}	SOC	C_{SH}	C_{HA}	C_{FA}	C_{HA}/C_{FA}
		g·kg^{-1}	% of SOC			
Shelterbelt	62.81	16.72	65.55	27.05	38.51	0.70
0-6	58.62^{a}	14.85^{a}	67.31^{a}	31.05^{a}	36.33^{a}	0.89^{a}
6-12	52.97^{a}	14.34^{a}	55.61^{ab}	30.38^{a}	25.30^{ab}	1.22^{a}
12-18	47.39^{b}	13.29^{a}	47.55^{ab}	30.46^{a}	16.95^{ab}	1.82^{a}
Control	46.69^{b}	14.26^{a}	36.76^{b}	24.50^{a}	12.36^{b}	1.61^{a}

Means followed by the same letters do not differ significantly ($\alpha=0.05$). The Kruskal-Wallis test was used.

Table 3. Spearman's rank correlation coefficient (r_s) between distance from black locust trees and content of soil organic carbon (SOC), humic substances (C_{SH}), humic acids (C_{HA}), fulvic acids (C_{FA}), and C_{HA}/C_{HF} ratio in cultivated soil.

Soil properties	SOC pools	SOC	C_{SH}	C_{HA}	C_{FA}	C_{HA}/C_{FA}
r_s	-0.7117*	-0.3706	-0.9021*	-0.4126	-0.8671*	0.8182*

*significant at $\alpha=0.05$

absorbance ratio at 465 nm and 665 nm) and ΔlogK (calculated as log K_{400nm} – log K_{600nm}) was done. Spectrophotometric measurements in the UV-VIS range were performed using the computerized double-beam spectrophotometer UV-VIS SPECORD M-42 with START software (Carl Zeiss Jena). Absorbance was measured separately in two ranges: UV – (230-400 nm) and VIS – (380-750 nm).

Determined results were aggregated into 4 groups (zones) according to the distance of the zone to the trees: 0-6, 6-12, and 12-18 m and the control (18-24 m). The mean values for these zones were calculated and the significance of differences between them was evaluated using the Kruskal–Wallis one-way analysis of variance by ranks. Correlation Spearman's rank (r_s) at $\alpha=0.05$ was used to evaluate the dependence between the main studied parameters and the distance from trees. Statistical analysis was made using Statistica 10.0 software. The contour map of organic carbon pools was created in Surfer 8.0 software using a kriging method.

Results and Discussion

Organic carbon content is mainly connected with soil type, texture, and land use [17]. Organic carbon in agricultural soil is mainly a result of tillage methods, while in forest soil, organic carbon in the humus layer is related to the impact of the organic horizon [18]. Samples taken from the cultivated soil, were characterized by SOC ranging from 14.26 to 14.85 g·kg^{-1} (Table 2).

Arable soil is usually characterized by a lower content of carbon in the A horizons compared with the corresponding horizons of forest soil [6, 8, 15]. The studied soil showed a similar arrangement: soil under the shelterbelt contained a higher amount of organic carbon compared to the cultivated soil. Shelterbelts play a role that is comparable to that of a forest.

It has been previously reported [2, 19, 20] that planting black locust trees can positively increase SOC content. A 50-year-old locust can increase soil up to 3 times that of agricultural soil, compared to soil areas covered with 5-year-old individuals of this species [19]. In both laboratory and field experiments, the fallen leaves of black locust were found to be the most important factor for the increase of carbon content in the soil [4]. Cultivated soil in the vicinity of the trees had the general condition quality of arable soil, but also was comparable to forest soil. The annual supply of organic matter in the form of leaves, flowers, and trees was limited mainly to the "edge" zones. Organic matter that gets mixed with the soil through tillage plays a similar role to green manure or compost [5].

Significantly higher C pools were found in zone 0-6 m than in zone 12-18 m and in the control. The pools of SOC decreased significantly as the distance from trees increased (Fig. 2, Table 3). Higher pools of SOC were characterized for the soil samples from under the shelterbelt compared to the cultivated soil samples.

There was a higher annual rate of SOC pools under the shelterbelt amounting to 0.32 Mg·ha^{-1}. The rate is comparable to that given by Post and Kwon [21], who presented the annual rate of change of SOC pools in a temperate region due to forestation of previously agricultural soils, as ranging between -0.086 Mg·ha^{-1} and 0.617 Mg·ha^{-1}. In China, forest soil covered with 20-year-old black locust trees was characterized by carbon stocks in the 0-20 cm layer, 22.36 Mg·ha^{-1}, giving an annual increase equal to 1.11 Mg·ha^{-1} [3]. Other studies conducted in China reported an increase in carbon pools in the 0-20 cm soil layer covered with 21- and 51-year-old black locust trees, to be

2.73 and 9.18 Mg·ha^{-1}·year^{-1}, respectively [22]. The determined annual increases in C stocks are much lower compared to the over 10-year-old black locust fuel wood plantation in Germany [2].

The difference between the pools of organic carbon in the cultivated soil adjacent to the trees (0-6 m) and the control was 11.9 Mg·ha^{-1}. Thus, the calculated annual increase in resources was 0.23 Mg·ha^{-1}·year^{-1}. A much lower level of carbon stock increments in agriculturally used soil than under the shelterbelt is caused by periodic soil structure degradation due to mechanical tillage, and a higher decomposition rate of physically protected organic matter in microagregates [15].

The intensive agricultural production in combination with the very good water-air properties of chernozem and a high SOC content was associated with a relative small increase in carbon resources from the black locust effect. A conversion from arable-use properties to forest-like properties caused a new level of equilibrium to be established between organic carbon decomposition and the humification rate in this soil [17].

Humic substances (HS) are a widely distributed major component of soil organic matter. These substances are built of a heterogeneous system of molecules containing different aromatic and alipfhatic compounds, and different function groups [10]. Humic substances are operationally divided into 3 groups based on their solubility: HAs, FAs, and humins. Humins are most resistant to the decomposition compounds of HS, and play an important role as a factor in soil fertility. This role mainly has to do with water-holding capacity and sorption processes. In another study, a higher amount of humins in soil as a function of inverse distance from black locust trees was presented [13]. In our study, the content of humins was not included.

The content of humic substances (C_{HS}) and HAs (C_{HA}), relative to organic carbon, is considered a measurement parameter of the degree of humification [18]. The yield of extracted humic substances (C_{HS}) varied in studied zones. The largest yield of C_{HS} (67.31%) in the 0-6 m zone had a significantly higher yield compared to the control soil (36.76%). As distance from trees increased, HS content was found to be significantly lower (r_s =-0.9021) (Table 3). In comparison, soil under the shelterbelt contained a slightly lower amount of HS in SOC compared to zone 0-6 m of the cultivated field.

The highest yield of HAs (C_{HA}) were obtained where the soil was adjacent to the shelterbelt (31.05%). The content of fulvic acids (C_{FA}) gradually declined as the distance from the trees became greater (r_s=-0.8607).

A significantly higher yield of HS in the 0-6 m zone, compared with the control, means a higher resistance against microbial decomposition. In addition, inputs of nitrogen from fallen leaves or other above-ground organs of black locust on the soil surface stimulate better conditions for the process of humification [1, 4]. However, higher HS content is connected with higher amount of FAs and a decrease in the C_{HA}/C_{FA} ratio.

A rapid decomposition process of aboveground organs (leaves and flowers) in soil is characteristic for the black locust. Lignin and polyphenol contents play a crucial role in the decomposition process of plant residues (leaves). In the case of the black locust, the lignin and polyphenol contents are large. Polyphenols are highly resistant to decomposition. Proteins and polyphenols together are able to form stable complexes in soil. These compounds from fresh organic matter incorporated in soil, cause recalcitrant carbon accumulation in soil as a long-term effect. The compounds also cause a high availability of nitrogen pools [23].

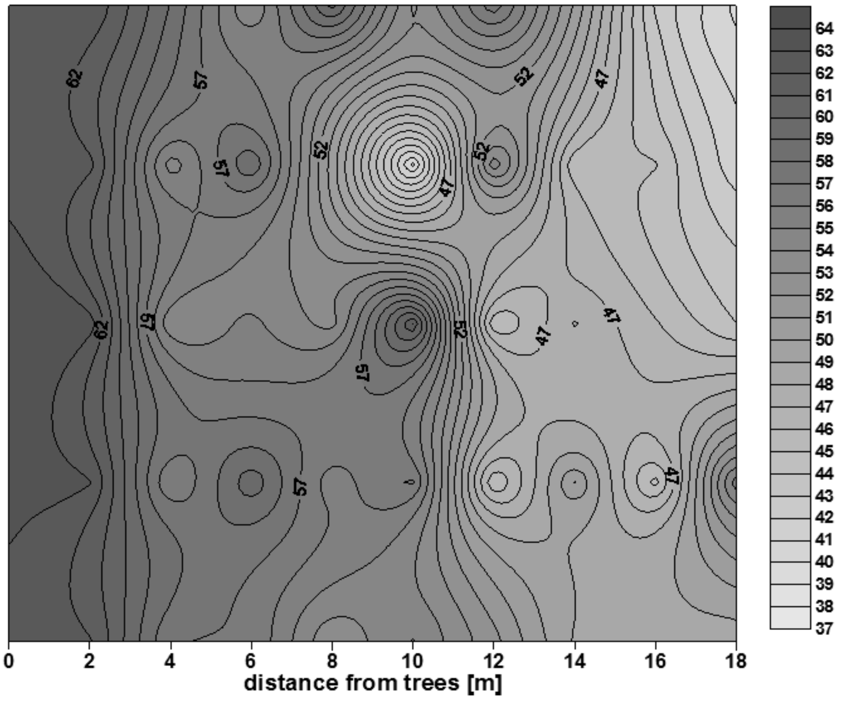

Fig. 2. Organic carbon pools in studied soils in Mg·ha^{-1}.

Table 4. Elementary composition of HAs and atomic ratios.

Distance from trees [m]	C	H	N	O	O/H	O/C	H/C	ω
	% w/w							
Shelterbelt	54.00	3.45	4.23	38.31	0.475	0.532	1.12	0.119
0-6	54.96^{a}	3.35^{a}	4.36^{a}	37.34^{a}	0.464^{a}	0.510^{a}	1.10^{a}	0.125^{a}
6-12	54.18^{a}	4.09^{a}	4.47^{a}	37.26^{a}	0.463^{a}	0.520^{a}	1.12^{a}	0.133^{a}
12-18	52.91^{a}	3.97^{a}	4.31^{a}	38.81^{a}	0.482^{a}	0.552^{a}	1.14^{a}	0.170^{a}
Control	51.97^{a}	4.25^{a}	4.22^{a}	39.57^{a}	0.491^{a}	0.571^{a}	1.16^{a}	0.188a

Means followed by the same letters do not differ significantly (α=0.05). The Kruskal-Wallis test was used.

Table 5. Spearman's rank correlation coefficient (r_s) between distance from black locust trees and chosen properties of HA in cultivated soil.

Soil properties	O/H	O/C	H/C	ω	$E_{2/4}$	$E_{4/6}$	ΔlogK
r_s	0.4545	0.4196	0.3916	0.4336	0.6923*	0.0490	-0.0839

*significant at α=0.05

The C_{HA}/C_{FA} ratio is considered to be a degree of the humification process of organic matter. In the upper horizons of rich-humus soil, the value of the C_{HA}/C_{FA} ratio is generally higher than 1. A higher degree of humification in the chernozem compared to other soil types was previously reported [9].

This parameter was higher as the distance from the black locust trees became greater (r_s=0.8182). In our study, the soil under the shelterbelt was characterized by lower values of the of the C_{HA}/C_{FA} ratio compared to the cultivated soil of the control.

The presence of older trees was probably the reason for the higher content of FAs as well as the reason for a lower C_{HA}/C_{FA} ratio near trees in the cultivated soil. In addition, different spatial arrangements of the C_{HA}/C_{FA} ratio can be affected by differences in the properties of the soil type, age, and species of trees. The more mature trees produced greater amounts of organic matter. Through decomposition processes, this greater amount of organic matter results in a greater amount of FAs in humic substances [24].

In agroecosystems adjacent to a shelterbelt, plant debris derived from crops and/or trees, enters the soil. The decomposition process is not only associated with the tree species, but the rotation of different crops is also involved. During the decomposition of plant residues in soil rich in nitrogen, the C_{HA}/C_{FA} ratio may not change. The decomposition of black locust residues rich in lignin, however, may show a C_{HA}/C_{FA} ratio rise due to the increased content of HAs [18].

HAs are heterogeneous compounds of HS that have a specific structure [16]. All analytical approaches in chemical composition studies of HAs only allow for the content determination of the guide structure of the individual elements or groups that can be identified.

The studied soil samples were characterized by different chemical compositions of the HAs (Table 4). The highest values of carbon content and the lowest oxygen content were determined in the samples of cultivated soil collected up to 6 m from trees (Table 5). Carbon content in the molecules of the HAs in mineral soil fluctuates between 53.8% and 58.7%, and oxygen from 32.8% to 38.3%. As the humification process advances, mature and stable HAs show a higher content of carbon and aromatic C-compounds [18]. According to Kleber and Johnson [25], an oxygen decrease in HAs usually means a higher degree of HS resistance against decomposition. Studied chernozem showed a similar arrangement, but its HS characteristics seem to be more resistant to any significant change in chemical composition. Thus, the studied elemental composition of HAs in cultivated chernozem reflects the relatively high maturity of HAs in zone 0-6 m compared to that in the control.

The values of the atomic ratios allow for an estimation of the HAs structure by assessing the aromatic rings' degree of condensation (the ratio of H/C) and by assessing the degree of maturity (O/C, O/H, ω) [16]. The values of the atomic ratios can show not only the differences, but also the connections and changes in soil humus.

There were lower values of atomic ratios O/C, O/H, H/C and internal oxidation (ω) of humic acids in soil in the vicinity of the shelterbelts (zone 0-6 m) compared with the control.

The value of the H/C ratio is inversely proportional to the aromatic rings' degree of condensation and is a measure of the aromaticity of HAs. According to a Barancikova [26] study, the H/C ratio value in the chernozems did not exceed 0.70. The obtained values indicated that isolated HAs are an aromatic system linked to an aliphatic chain containing up to 10 carbon atoms [18]. The mineral nitrogen supply, according to Szajdak et al. [1], results in a higher concentration of aromatic chains in HA molecules. A higher nitrogen content in soil from the decomposition of black locust leaves and other plant debris is comparable to the application of nitrogen in a green manure form.

The mean internal oxidation values (ω) can be helpful when determining the humification of the organic substances that had been freshly introduced into the soil, and when determining the characteristics of formed HAs [16]. The lowest values of ω in the soil immediately adjacent to the trees are associated with higher nitrogen content. The degree of internal oxidation shows lower values in soil fertilized with manure or nitrogen. Moreover, partial oxidation of HAs is a characteristic feature of soil used for agricultural purposes [27].

The spatial arrangement of the atomic ratios can be better understood using the van Krevelen diagram, which presents the relationship between the H/C and O/C ratio (Fig. 3). The humic acids isolated from the cultivated soil adjacent to the black locust shelterbelts and from soil under the trees are in the lowest position on the diagram. Opposite to them are the control and samples from a distance of 12-18 m from shelterbelts. Based on this diagram, it can be concluded that the most mature and the most stabilized HAs are those in the soil located directly adjacent to the trees. In addition, the direction of change leading to the stability is seen to be primarily through a process of carboxylation and of the second row dehydrogenation process [27]. Putting into the soil organic black locust material, a high amount of lignin and nitrogen, and the nitrogen fertilization used in crop cultivation makes the HAs in soil adjacent to the trees more mature [1].

The $E_{2/4}$ parameter values are inversely proportional to the degree of HS maturity. In the soil profile, this maturity value refers to the constant supply of organic matter, which generally decreases according to depth [18]. The $E_{2/4}$ parameter range in the cultivated soil was 4.09-4.27 (Table 6). The obtained parameter in soil under the shelterbelts, amounted to 4.20. The shaped spatial distribution of parameter values was significantly lower in the immediate vicinity of the trees (r_s =0.6923) (Table 5).

The values of the $E_{4/6}$ for the studied cultivated soil ranged 3.57-3.67. The parameter was higher under shelterbelts than in the cultivated soil (3.70).

$E_{4/6}$ varies depending on soil type and land use, and is not directly related to the relative content of condensed aromatic rings. Moreover, $E_{4/6}$ is negatively correlated with size, mass of HAs molecules, and aromaticity [18].

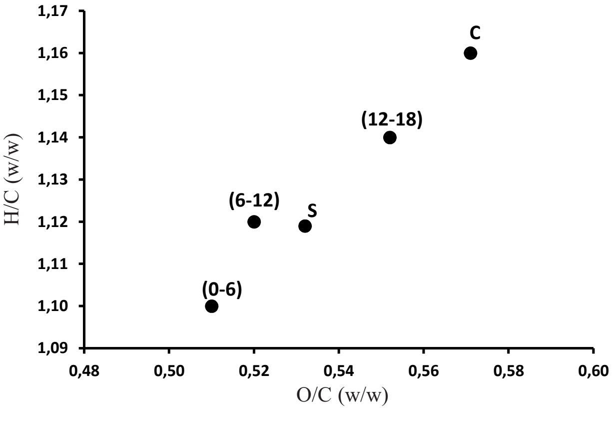

Fig. 3. H/C versus O/C for HAs (van Krevelen's diagram). Distance from shelterbelt is given in brackets. C – control, S – shelterbelt.

Table 6. Spectral ratios of HAs in the investigated soils.

Distance from trees [m]	$E_{2/4}$	$E_{4/6}$	ΔlogK
Shelterbelt	4.20	3.70	0.557
0-6	4.09^a	3.62^a	0.545^a
6-12	4.10^a	3.57^a	0.542^a
12-18	4.12^a	3.62^a	0.544^a
Control	4.27^a	3.67^a	0.557^a

Means followed by the same letters do not differ significantly (α=0.05). The Kruskal-Wallis test was used.

In this study, the obtained values of the $E_{2/4}$ and $E_{4/6}$ ratios prove a high advancement of the humification process in soil samples taken from the chernozem humus layer. Low $E_{4/6}$ indicates a high HS quality, which is typical for chernozem soil [26].

The reason for lower $E_{4/6}$ results in zone 0-6 m compared to control is most likely due to the larger size and molecular mass of the HAs. Lower values of $E_{4/6}$ may result from the use of high doses of mineral nitrogen fertilizer or manure. According to Barancikova [26], the parameter in the chernozem is lower than 4.5.

Black locust shows a high lignin fraction in leaflets and has a high potential to form recalcitrant humus compounds during decomposition in comparison with other species. In addition, lignin-derived phenols can be physically protected from oxidation in soil in silt-size fractions mainly. This factor can be important in studied loess soil where the amount of this fraction is large [28].

The degree of humification, according to Kumada, shows a close relationship with the value of ΔlogK parameter: the more advanced the humification process; the lower the coefficient. HAs extracted from all the studied soils were counted as A types, i.e. to the HAs with high stability, where the value is lower than 0.6. In the A types, there is a higher amount of C and a lower amount of O in the molecule. These amounts of C were especially observed in zones adjacent to trees [29].

Cultivated soil samples were characterized by relative lower values of ΔlogK (0.542-0.557). The parameter was close in 3 zones (0-6, 6-12, and 12-18), and the value was lower compared to the control. Under the shelterbelt, equal values were determined compared to the control.

The values of this parameter in the studied cultivated soils, are lower compared with the characteristics of HAs in forest mineral layers [18]. Values equal to the highest values obtained in cultivated soil within the plot were found under the shelterbelt. Higher values are due to the nature of the HAs optical properties. A constant supply of organic matter means a less mature nature is exhibited. Lower values of the coefficient in the chernozem soil type, in comparison to other soil types, were also found in previous studies [9].

Table 7. Spearman's rank correlation coefficient (r_s) between chosen chemical and spectral parameters of HAs in cultivated soil.

Properties of HA	O/H	O/C	H/C	ω	$E_{2/4}$	$E_{4/6}$	ΔlogK
O/H	-	0.9930*	0.9790*	0.9790*	0.3357	0.4126	0.2378
O/C	0.9930*	-	0.9860*	0.9860*	0.3427	0.3497	0.2238
H/C	0.9790*	0.9860*	-	0.9860*	0.3357	0.3427	0.2517
ω	0.9790*	0.9860*	0.9860*	-	0.4126	0.3916	0.3217
$E_{2/4}$	0.3357	0.3427	0.3357	0.4126	-	0.1888	0.8881*
$E_{4/6}$	0.4126	0.3497	0.3427	0.3916	0.1888	-	0.4615
ΔlogK	0.2378	0.2238	0.2517	0.3217	0.8881*	0.4615	-

* significant at α=0.05

Spatial values prove that more mature HAs were characteristic for zones close to the shelterbelt. The ΔlogK values were proportional to the $E_{2/4}$ coefficient values, as stated in previous studies (Table 7) [30].

Conclusions

1. The content and pools of organic carbon were the highest in samples taken from the farmland closest to the black locust trees and can be treated as an important factor of carbon stock increments in soil.
2. As distance from trees increased, content of humic substances and fulvic acids was found in cultivated soil to be significantly lower.
3. C_{HA}/C_{FA} ratio in cultivated soil was higher as the distance from the black locust trees became greater.
4. Based on the van Krevelen diagram, it can be concluded that the most mature and the most stabilized humic acids are those in the cultivated soil located directly adjacent to the trees.
5. The shaped spatial distribution of $E_{2/4}$ parameter values was significant lower in the immediate vicinity of the trees due to a constant supply of organic matter in the soil.

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