



Humic substances and aggregate stability in rhizospheric and non-rhizospheric soil

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Abstract

Purpose The paper describes rhizospheric (Rs) and non-rhizospheric (nRs) soil to demonstrate the zone of the plant root impact on physical and chemical properties of the soil. The effects of the process accompanying the transformations of organic matter into humic substances in the rhizosphere of “common dandelion” *Taraxacum officinale* have been determined, and the properties of humic acids (HAs) were described. The importance of iron and clay minerals for the formation of a stable and water-resistant soil structure has been emphasized.

Materials and methods The laboratory analysis involved determination of basic physical and chemical soil properties: texture, pH, cation exchange capacity (CEC), electrical conductivity, and content of total organic carbon (TOC) and dissolved organic carbon (DOC) and quality of humic substances: optical properties of HAs and its separation into hydrophilic (HIL) and hydrophobic (HOB) fractions, speciation of iron, glomalin operationally described as an easily extractable glomalin-related soil protein (EE-GRSP), and soil aggregate stability (SAS) of six size classes of soil aggregates.

Results and discussion The Rs was reported with a higher TOC and DOC content (measured in the CaCl₂ extracts), however not significantly. The HAs isolated from Rs revealed a significantly higher content of humic substances at its initial decomposition stage, as compared with nRs. A significantly higher concentration of EE-GRSP was noted in the aggregates of the rhizospheric zone (mean 1.14 g kg⁻¹) than in the aggregates collected from root-free soil (mean 0.94 g kg⁻¹). There was noted the highest mean share of 1–3 mm soil aggregates in Rs as well as in nRs, respectively 44.4 and 38.3%. The soil material both in Rs and in nRs contained high amounts of exchangeable Ca²⁺, and smectite is the predominant clay mineral. It was favorable for the accumulation of organic carbon and for the formation of good soil physical condition (tilth). Higher but insignificant SAS values were observed for Rs (mean SAS = 95.6%) than for nRs (mean SAS = 93.9%).

Conclusions The studies confirm the role of common dandelion roots in the process of organic carbon accumulation in rhizospheric zone and a favorable effect on the mechanism of the formation of water-resistant aggregates. Higher values of SAS for the Rs were affected by the content of TOC, DOC, exchangeable Ca²⁺ and the concentration of EE-GRSP, and, less considerably, the content of Fe and clay minerals.

Keywords Glomalin · Humic substances · Rhizospheric and non-rhizospheric soil · Soil aggregate stability · Total and dissolved organic carbon

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1 Introduction

The role of soil organic matter (SOM), including humic substances, in terms of soil formation and development, is unquestionable. Soil organic matter can be converted into inorganic constituents, and the carbon of organic residues can be transformed and converted to humic substances through biochemical and abiotic processes (Guggenberger 2005). SOM is responsible for improving soil tilth, pH buffering, and improving air-water relations

in soil, and it serves as a large pool of carbon and other plant essential nutrients (Schindler et al. 2007).

Among different SOM components, there are two important extractable fractions that might substantially affect soil properties. They are HAs and glomalin-related soil protein (GRSP) (Nichols and Wright 2005).

The HAs are built of structures with both hydrophobic and hydrophilic properties which determine, e.g., the solubility and the susceptibility of HAs to biodegradation and affect their sorption potential (Wen et al. 2007). By applying the high-performance liquid chromatography (HPLC) method, one can divide the molecules of HAs into fractions that are hydrophobic and hydrophilic in nature (Woelki et al. 1997; Preuße et al. 2000; Sierra et al. 2006; Dębska et al. 2010, 2012). An additional aspect of the study of HAs is the determination of the value of absorbance at 465 nm (A_{465}) and 665 nm (A_{665}) and the absorbance ratio $A_{4/6}$ (Jing-an et al. 2007; Kalembasa and Becher 2009; Kondratowicz-Maciejewska et al. 2011) which can be used to estimate the maturity of the HAs (Polak et al. 2011) and as an indicator of the degree of organic matter humification. The absorbance at 465 nm reflects the organic material at the beginning of humification, whereas the absorbance at 665 nm indicates on the strongly humified material with a high degree of condensation of aromatic constituents (Albrecht et al. 2011). Content of SOM at the initial phases of decomposition is confirmed by the aliphatic structure of HAs (Xiang-yun et al. 2014). The Vis parameters are correlated with the key properties of humic substances such as aromaticity and molecular weight. The $A_{4/6}$ ratio is inversely related to the degree of aromaticity, molecular weight, and acidity of HAs (Rodríguez et al. 2016).

The most mobile part of organic matter includes carbohydrates, proteins, hydrocarbons, and other organic compounds, soluble in water or in salt solutions with neutral reaction. In terms of ecology, a very important role in the soil environment is played by the most mobile and easily decomposing humic substances fraction-dissolved organic matter (DOM) (Gonet and Dębska 2006; Kondratowicz-Maciejewska 2007). Kalbitz and Kaiser (2008) claim that probably the most stable part of DOM are aromatic compounds. Dissolved organic matter is also a factor stabilizing colloids and soil aggregates (Kalbitz et al. 2000). DOM is the source of nutrients and energy for microorganisms (Haynes 2005; Voroney et al. 2007). The amount of bacteria, actinomycetes and fungal species are usually greater in the rhizosphere than in root-free soil (Giri et al. 2005). Glomalin is a glycoprotein produced by the arbuscular mycorrhizal fungi (AMF) in the phylum Glomeromycota which colonize the roots of a majority of plants (Janos et al. 2008). The overall effect of hyphal enmeshment and C inputs can be a significant increase in soil structural stability, which is also affected by the host/fungal combination (Piotrowski et al. 2004). Glomalin and glomalin-related proteins secreted by AMF into the soil could be crucial for soil aggregation process

(Bedini et al. 2009). Fungal hyphae improve aggregate stability by reorientation of clay particles, binding particles with extracellular polysaccharides (Ternan et al. 1996), they also may indirectly improve soil aggregate stability by providing carbon for other microorganisms which produce soil binding chemicals. Soils rich in swelling clays have more total glomalin than soils containing low-activity clays since hydrophobic, recalcitrant nature of glomalin may protect other aggregating agents (Wright and Upadhyaya 1996). The researches revealed that glomalin concentration in soil is highly correlated with the presence of water-stable aggregates as well as with the content of soil carbon (Borie et al. 2006; Wright et al. 2007; Kohler et al. 2010; Tobiašová 2011; Šimanský et al. 2013).

Humic substances are recognized as the most important component of soil as they influence the soil structure and play the main role in the chelation of mineral elements. The structure, which shows important effects on the physical properties of soil, is often measured by the stability of soil aggregates (Six et al. 2000; Bronick and Lal 2005). Soil aggregate stability is a crucial soil property affecting soil sustainability (Amézketa 1999). The size distribution and stability of soil aggregates positively correlates with the SOM and clay minerals (Tisdall and Oades 1982; Six et al. 2004). There was also found a positive relationship between the stability of soil aggregates, cation exchange capacity (CEC), and the content of humic substances (Oades 1984; Six et al. 2002; von Lützwitz et al. 2006; Bartlová et al. 2015). The stability and size distribution of soil aggregates is also affected by land use (Zhao et al. 2017) and rate of decay of macro- and microaggregate is highly influenced by the intensity of tillage (Al-Kaisi et al. 2014). Additionally, it was found that rhizosphere aggregates are more stable than non-rhizosphere soil aggregates (Caravaca et al. 2002). Furthermore, it was also demonstrated that iron oxides act as cementing substance in soil aggregates > 0.5 mm; however, within different size fractions of soil aggregates, the correlation with Fe was inconsistent. For the smaller aggregates (0.5–0.25 and < 0.25 mm), significant interaction was not found (Zhao et al. 2017). Barral et al. (1998) showed that the water stability of soil aggregates is attributed to the high organic matter and Fe contents. Iron (hydr)oxides have been observed to stimulate aggregation; however, poorly crystalline and amorphous iron (Fe_o) is more effective than free iron (Fe_d) at stabilizing soil aggregates (Oades and Waters 1991; Duiker et al. 2003). Transformations of iron in the soil can be inferred from the ratio of oxalate to dithionite-extractable iron (Fe_o/Fe_d), which defines the relationship between the content of the most active forms of iron and its non-silicate forms (Schwertmann 1988). The presence of Fe minerals and exchangeable cations such as Ca^{2+} and Mg^{2+} leads to accumulations of organic C in soils (Oades 1988).

We have hypothesized that the formation of soil aggregates is determined by soil organic matter, which is affected by the

processes in rhizospheric zone of common dandelion, while iron oxides and clay minerals are the factors providing the stability of aggregates. To demonstrate the effect of plant roots on the transformation of organic matter into humic substances and the formation of a stable aggregate structure, the physical and chemical Rs properties of common dandelion (*Taraxacum officinale*) with the parameters of root-free soil were compared. Common dandelion is a perennial mycotrophic weed and a good companion plant in pastures and meadows; however, it develops an extensive root system and, in the next years, it may begin to compete with the main crop. Its taproot will bring up nutrients for shallow-rooting plants and add nitrogen to soil environments. Common dandelion also has a beneficial effect on mycorrhizal colonization, P content and growth of a subsequent plant crop (Kabir and Koide 2000).

2 Materials and methods

The research covered the floodplain area between the Vistula riverbed and the flood embankment within the Grudziądz Basin (the Lower Vistula River, north of Poland). The area is a farmland with cereal, beetroot, potato growing, and cattle grazing. The bedrock of this region consists of Quaternary alluvial deposits. The predominating soils in the study area are Gleyic Fluvisols (IUSS Working Group WRB 2015). The research involved 20 soil samples and compared the properties of 10 samples from rhizospheric (Rs) and 10 samples from non-rhizospheric (nRs). In the soil samples, the basic physical and chemical properties were assayed. The Rs consisted of the soil material from common dandelion roots (*Taraxacum officinale*). The Rs was sampled at a distance < 5 mm adjacent to the roots (i.e., collecting the soil aggregates falling off when shaking the root system), and then, fine roots and other plant debris were removed.

The nRs was sampled 1 m away from the common dandelion (0–20 cm deep). Prior to analysis, the soil samples were sieved through 2 mm sieve for physical and chemical analysis and through 6 sieves (7, 5, 3, 1, 0.5, and 0.25 mm) for aggregate stability.

The selected properties of Rs and nRs samples were determined with commonly applied methods. Soil pH was measured potentiometrically using pH meter equipped in glass electrode in 1 M KCl solution (1:2.5 soil-solution ratio). The content of calcium carbonate was determined using the Scheibler apparatus (the content of CaCO₃ was calculated from volume of emitted carbon dioxide as a consequence of reaction with 10% HCl). Electrical conductivity (ECe) was determined in a 1:5 soil/distilled water suspension. To determine the exchangeable cations (Ca²⁺, Mg²⁺, K⁺, Na⁺), the soil was saturated with 0.1 M BaCl₂ solution (PN-EN ISO 11260 2011). Concentration of Ca, Mg, K, and Na were determined using Philips PU 9100X spectrometer. Total exchangeable

bases (TEB) were calculated by adding the content of exchangeable cations.

Soil total organic carbon, total nitrogen (Nt), and dissolved organic carbon (DOC) were determined with Vario Max CN-Elementar Analysensystem GmbH analyzer. The amount of DOC was measured in the solutions obtained after extraction with 0.004 M CaCl₂ (1:10 w/v soil:extractant ratio, 1 h shaking). The HAs were separated following the Schnitzer (1978) method. For HAs, the optical properties in the VIS range with Lambda 20 spectrophotometer, Perkin-Elmer, were determined. With the values of absorbance, at wavelengths of 465 nm (A_{465}) and 665 nm (A_{665}), there were calculated values of coefficient: $A_{4/6}$ —ratio of the value of absorbance at wavelength of 465 and 665 nm. The values of absorbance at the wavelength of 465 nm (A_{465}) point to the presence of humic substances at the initial stage of humification, whereas for the wavelength of 665 nm (A_{665}) to the humic substances with a high degree of humification.

The HAs were separated into HIL and HOB fractions with a liquid chromatograph (HPLC series 200, Perkin-Elmer). The separation involved the use of column X-Terra C18, 5 μ m, 250 \times 4.6 mm. Solutions of HAs were applied in 0.01 M NaOH at the concentration of 2 mg mL⁻¹ of HAs, injection of the sample 0.1 mL, solvent: acetonitrile-water, solvent flow in the gradient (ratio H₂O: ACN (v/v) over 0–6 min (99.5:0.5), 7–13 min (70:30), 13–20 min (10:90), and detection at the wavelength of 254 nm. Based on the areas determined under peaks, the share of HIL (first peak on the chromatogram) and HOB (second peak on the chromatogram) fractions in humic acids molecules and the parameter HIL/HOB were determined (Woelki et al. 1997; Preuße et al. 2000).

The easily extractable glomalin (EE-GRSP) was extracted from soil samples according to the procedure described in detail elsewhere (Wright and Upadhyaya 1996; Wright et al. 2006). Soil extraction includes autoclaving of weighed sample in a solution of sodium citrate. Briefly, the extraction process consists of the following steps: weighing 1 g of soil and placing it in the 50 mL PP centrifuge tube, adding 20 mM sodium citrate (pH 7.0), autoclaving ($t = 121$ °C, $p = 1.4$ kg cm⁻¹), centrifuging and decanting of the supernatant. The absorbance of extracts was measured at 595 nm by UV-VIS Smartspec spectrophotometer (Bio-Rad 170-2525).

Particle-size distribution was determined applying the areometric Casagrande method in Prószyński's modification. Soil suspension density is measured at regular time intervals from the start of sedimentation at constant temperature (PN-ISO-11277: 2005). The content of free iron oxides (Fe_d) in the dithionite-citrate extract was determined by Mehra and Jackson (1960) method, while the content of amorphous iron oxides in the ammonium oxalate extract (Fe_o) according to Tamm's method, modified by Schwertmann (1964). The measurement of the Fe content was performed by applying the atomic absorption spectrometry method (AAS), using

Philips PU 9100X spectrometer. Based on the content of Fe_d and Fe_o , the content of crystalline iron oxides (Fe_c) was calculated using the formula: $Fe_c = Fe_d - Fe_o$.

Separation of clay fraction ($\phi < 2.0 \mu\text{m}$) was performed according to Jackson's (1975) method. Prior to the separation, organic matter and free iron oxides were removed (using 30% H_2O_2 and citrate-bicarbonate-dithionite, respectively). Following a dispersion of the suspension with Na-ionite, the clay fraction was separated with the accelerated sedimentation method using the centrifuge. Clay samples were saturated with Mg^{2+} and K^+ . Oriented clay mounts (on glass slides) were analyzed using X-ray diffraction (XRD) method. The air-dried Mg-saturated samples were analyzed at 25 °C followed by ethylene glycol solvation. The air-dried K-saturated samples were analyzed at 25 °C and then heated at 550 °C. XRD analyses were performed using the X'Pert Powder diffractometer operating at 40 KV and 30 mA with $CuK\alpha$ radiation. Clay mineral identification was made according to the position of basal reflections (Brindley 1980; Brown and Brindley 1980; Borchardt 1989). The clay mineral proportions were estimated from the ethylene glycol-solvated pattern. Semi-quantitative estimates of the proportions of clay minerals were derived from integrated peak area. The XRD patterns were processed using the ORIGIN software.

Prior to the aggregate stability analysis, the air dried samples of soil were sieved to separate six size classes of aggregates: > 7 , $7-5$, $5-3$, $3-1$, $1-0.5$, and $0.5-0.25$ mm. Each fraction of aggregates was individually collected. Based on each aggregate size class weight, their proportion to the bulk soil sample was calculated. The aggregate stability of particular size-classes was measured in the wet-sieving apparatus (Eijkelkamp 08.13) on the 0.25 mm screens. The stability of soil aggregates was tested in four replications. The samples of aggregates were pre-moistened for 10 min before submerging. Then, the sieves were placed in the apparatus sieve holder over the cans with distilled water. The samples were wet-sieved for 3 min (1.3 cm stroke, 34 oscillations per minute). Soil particles which passed through the sieve were dried at 105 °C and weighed. The resistant soil material on each sieve was dispersed with 0.1 M tetrasodium pyrophosphate ($Na_4P_2O_7$), dried at 105 °C, and weighed. The stable fraction is equal to the weight of the material obtained in the dispersing solution cans (A) divided by the sum of weights obtained in the dispersing solution cans and distilled water cans (B). The mass of $Na_4P_2O_7$ was subtracted from the weight of dried, dispersed soil material. The soil aggregate stability index (SAS) was calculated according to the formula:

$$SAS = \frac{A}{A + B} \cdot 100\%$$

The soil properties were treated with standard statistics and statistical tests (ANOVA). The significance of the differences

between means was evaluated drawing on the Tukey test for uneven numbers. Pearson's correlation analysis was also performed for the soil properties. The statistical analyses were made using Statistica 10.0 (StatSoft Inc., Tulsa, USA).

3 Results

The Rs and root-free zone are medium- to fine-textured soils (Table 1) developed from recent alluvium. The mean content of the sand fraction (2.0–0.05 mm) in Rs accounted for 40.8%, silt fraction (0.05–0.002 mm) 40.3%, and clay fraction (< 0.002 mm) 18.9%, and it was similar to the content in nRs: 44.2, 39.0, and 17.1%, respectively (Table 2). The nRs soil contained a significantly higher content of Fe_d (6.9–16.4 $g\ kg^{-1}$) and Fe_c (3.2–10.4 $g\ kg^{-1}$) as compared to Rs (Fe_d 4.4–10.1 $g\ kg^{-1}$ and Fe_c 1.7–4.7 $g\ kg^{-1}$) (Fig. 1). The average value of the ratio Fe_o/Fe_d was 0.44 for nRs and 0.55 for Rs (Table 3). The statistical analysis of the results showed that Fe_o was significantly ($P < 0.05$) correlated with the content of clay fraction both in nRs and in Rs (Table 4). The clay fraction ($< 2.0 \mu\text{m}$) of Rs (from 9 to 29%) and nRs (from 9 to 27%) is predominated by smectite with illite, illite-smectite, kaolinite (Fig. 2), and vermiculite as admixtures (Table 1). The pattern of ethylene glycol-treated clay fraction indicated presence of smectite group minerals with sharp peak $d = 1.703$ nm in Rs-6 and $d = 1.701$ nm in nRs. Illite is also present (peaks at 1.000; 0.499; 0.334 nm), as a kaolinite (peak at 0.712 and 0.357 nm) (Fig. 2).

The pH value of the Rs of common dandelion as well as nRs ranged from pH 6.63 to 7.17 and from pH 6.63 to 7.11, respectively, and it varied inconsiderably, which is seen from a very low value of the coefficient of variation (CV) (Table 3). The soil pH was affected by the content of $CaCO_3$, and the average content of which (7.4 $g\ kg^{-1}$) was higher in nRs than in Rs. The exchangeable cations were dominated by calcium. The mean content of Ca^{2+} in Rs and nRs was similar, and it was 29 $cmol_{(+)}\ kg^{-1}$ and 26 $cmol_{(+)}\ kg^{-1}$. Significant differences in the content (Table 2) of exchangeable K^+ ($P = 0.002$) and Na^+ ($P = 0.0002$) were noted; however, the parameters showed a considerable variation, especially in Rs (CV value 45 and 65%, respectively). The soils under study did not show salinity since the EC values were lower than 1 $dS\ m^{-1}$; nevertheless, in Rs, significantly higher values of electrical conductivity ($P = 0.001$) were observed.

The content of TOC and Nt in Rs ranged from 23.6 to 48.1 $g\ kg^{-1}$ and from 2.3 to 4.6 $g\ kg^{-1}$, respectively (Table 3). The lower values of those parameters were noted in nRs (21.4 to 39.1 $g\ kg^{-1}$ and 1.6 to 3.3 $g\ kg^{-1}$, respectively). The ratio of carbon content to nitrogen ranged from

Table 1 Texture and clay minerals of rhizospheric soil (Rs) and non-rhizospheric soil (nRs)

Samples	Sand 2.0–0.05 mm %	Silt 0.05–0.002 mm	Clay < 0.002 mm	Texture* (USDA)	Clay mineral composition
Rs-1	65	26	9	Sandy loam	S, I, K
Rs-2	32	43	25	Loam	S, I-S, I, K
Rs-3	23	53	24	Silt loam	S, I-S, I, K
Rs-4	39	40	21	Loam	S, I-S, I, K
Rs-5	40	43	17	Loam	S, I-S, I, K
Rs-6	45	36	19	Loam	S, I, K
Rs-7	38	47	15	Loam	S, I-S, I, K, V
Rs-8	21	50	29	Clay loam	S, I, K
Rs-9	52	33	15	Loam	S, I-S, I, K
Rs-10	53	32	15	Sandy loam	S, I-S, I, K, V
SD	13.6	8.56	5.93	–	–
CV (%)	33.4	21.3	31.4	–	–
nRs-1	72	19	9	Sandy loam	S, I, K
nRs-2	38	42	20	Loam	S, I, K, V
nRs-3	28	48	24	Loam	S, I-S, I, K
nRs-4	39	46	15	Loam	S, I-S, I, K
nRs-5	49	35	16	Loam	S, I-S, I, K
nRs-6	43	40	17	Loam	S, I-S, I, K
nRs-7	39	47	14	Loam	S, I-S, I, K, V
nRs-8	20	53	27	Silt loam	S, I, K
nRs-9	55	31	14	Sandy loam	S, I-S, I, K
nRs-10	59	29	15	Sandy loam	S, I, K, V
SD	15.2	10.4	5.26	–	–
CV (%)	34.4	26.8	30.8	–	–

SD standard deviation, CV coefficient of variation, S smectite, I illite, I-S illite/smectite, K kaolinite, V vermiculite

*Soil textural classes based on the United States Department of Agriculture (USDA 1987)

9.2 to 13.6. Similarly, the mean content of DOC in Rs was higher as compared to nRs (850 mg kg⁻¹ and 737 mg kg⁻¹, respectively). The amount of DOC in the TOC ranged from 2.1 to 3.6% in Rs and from 2.2 to 3.3% in nRs.

The HAs of the Rs showed a significantly higher intensity of the absorption at 465 and 665 nm, which were, on average, 4.93 and 0.76, as compared with the nRs, 3.49 and 0.56, respectively (Table 5). Significantly higher ($P = 0.019$) values of the coefficient of absorbance A_{466} (Table 2) were noted for the HAs of Rs.

Using a reversed phase chromatography method, the HIL and HOB fractions of HAs were obtained. Based on the areas determined under peaks, the amount of HIL and HOB fractions in HAs and the ratio HIL/HOB were defined (Fig. 3). The share of HIL fraction of HAs was higher, and it ranged from 65.6 to 77.5%, as compared to the share of HOB fraction (from 22.5 to 34.4%). In the HAs of Rs soil, a significantly lower amount of HIL fraction ($P = 0.003$) and significantly higher of HOB fraction ($P = 0.003$) in comparison with the HAs of nRs were

noted (Table 2). The values of HIL to HOB fractions ratio ranged from 1.91 to 3.59 (Table 5). Significantly lower values of the HIL/HOB ratio were noted for the HAs of Rs ($P = 0.002$) (Table 2).

The Rs contained a significantly ($P = 0.04$) higher mean EE-GRSP concentration (1.14 g kg⁻¹) than the nRs (0.94 g kg⁻¹) (Fig. 4). The results indicate also a significant positive correlation between the concentration of EE-GRSP and DOC: for Rs $r = 0.77$ and nRs $r = 0.66$, $P < 0.05$ (Table 4).

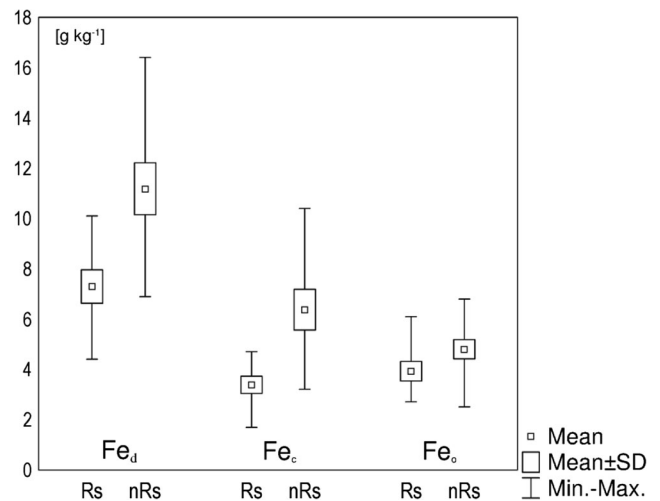
The highest mean contribution of 1–3 mm soil aggregates in Rs (44.4%) as well as in nRs (38.3%) was noted (Fig. 5). Moreover, in Rs, no aggregates > 7 mm were found, whereas their mean amount in nRs was 13.0%. The significant difference concerned the contribution of 3–5 mm soil aggregates, and their participation in Rs was 25.6% and in nRs 13.6% ($P = 0.0002$) (Table 2). The analyzed class of aggregates (7–0.25 mm) demonstrated a very high resistance against disruption when exposed to water (Table 6). Higher values of soil aggregate

Table 2 Results of statistical analysis (Anova, the Tukey test)

Parameter	Rs <i>n</i> = 10 Mean content	nRs <i>n</i> = 10 Mean content	Significant level (<i>P</i>)
Sand [%]	40.8	44.2	<i>P</i> = 0.66
Silt [%]	40.3	39.0	<i>P</i> = 0.76
Clay [%]	18.9	17.1	<i>P</i> = 0.48
Fe _d [g kg ⁻¹]	7.3	11.2	<i>P</i> = 0.006*
Fe _c [g kg ⁻¹]	3.4	6.4	<i>P</i> = 0.003*
Fe _o [g kg ⁻¹]	3.9	4.8	<i>P</i> = 0.12
pH	6.94	6.85	<i>P</i> = 0.25
CaCO ₃ [g kg ⁻¹]	5.3	7.4	<i>P</i> = 0.07
ECe [dS m ⁻¹]	0.52	0.32	<i>P</i> = 0.001*
Ca ²⁺ [cmol ₍₊₎ kg ⁻¹]	29.0	26.0	<i>P</i> = 0.49
Mg ²⁺ [cmol ₍₊₎ kg ⁻¹]	2.3	1.8	<i>P</i> = 0.24
K ⁺ [cmol ₍₊₎ kg ⁻¹]	0.2	0.5	<i>P</i> = 0.002*
Na ⁺ [cmol ₍₊₎ kg ⁻¹]	0.2	0.9	<i>P</i> = 0.0002*
TEB [cmol ₍₊₎ kg ⁻¹]	31.6	29.2	<i>P</i> = 0.52
TOC [g kg ⁻¹]	33.0	27.2	<i>P</i> = 0.06
Nt [g kg ⁻¹]	3.1	2.60	<i>P</i> = 0.10
DOC [mg kg ⁻¹]	850	737	<i>P</i> = 0.07
A ₆₆₅	0.76	0.56	<i>P</i> = 0.0003*
A ₄₆₅	4.93	3.49	<i>P</i> = 0.0001*
A _{4/6}	6.50	6.20	<i>P</i> = 0.019*
HIL [%]	70.4	74.8	<i>P</i> = 0.003*
HOB [%]	29.6	25.2	<i>P</i> = 0.003*
HIL/HOB	2.41	3.01	<i>P</i> = 0.002*
EE-GRSP [g kg ⁻¹]	1.14	0.94	<i>P</i> = 0.04*
Group of aggregates [%]			
> 7 mm	–	13.0	–
7–5 mm	3.0	5.8	<i>P</i> = 0.011*
5–3 mm	25.6	13.6	<i>P</i> = 0.0002*
3–1 mm	44.4	38.3	<i>P</i> = 0.21
1–0.5 mm	9.7	7.9	<i>P</i> = 0.16
0.5–0.25 mm	7.1	7.7	<i>P</i> = 0.75
< 0.25 mm	10.2	13.7	<i>P</i> = 0.35
SAS [%]			
7.0–0.25 mm	95.6	93.4	<i>P</i> = 0.11
7.0–5.0 mm	98.7	96.2	<i>P</i> = 0.25
5.0–3.0 mm	98.0	96.0	<i>P</i> = 0.40
3.0–1.0 mm	96.0	94.6	<i>P</i> = 0.56
1.0–0.5 mm	93.3	92.6	<i>P</i> = 0.74
0.5–0.25 mm	92.1	87.7	<i>P</i> = 0.35

*Significant differences

stability were determined for Rs than for nRs. The difference was non-significant; however, in comparison to nRs, the aggregates in rhizospheric zone were characterized by higher SAS mean values: 93.4 and 95.6%, respectively (Table 2).

**Fig. 1** The content of free Fe (Fe_d), amorphous Fe (Fe_o), and crystalline Fe (Fe_c = Fe_d - Fe_o) in rhizospheric soil (Rs) and non-rhizospheric soil (nRs)

4 Discussion

The texture of investigated soils varied from sandy loam to clay loam (Table 1). Aggregate stability is determined by the spatial arrangement of constituent particles and the nature of their interactions. Soil tilth is influenced both by soil texture and by soil structure. Fine particles and Fe_o, especially contributed to the formation of water stable aggregates both in analyzed Rs and nRs. Duiker et al. (2003) demonstrated that poorly crystalline iron oxides are more effective than free Fe in stabilizing soil aggregates. The content of Fe_c was significantly lower in Rs in comparison with nRs, which indicates that humic substances can inhibit crystallization of iron oxide. The conversion of amorphous iron oxides into the crystalline ones is slowed down by the increased presence of organic matter in soil (Schwertmann et al. 1986). Humic substances may act as electron carriers for ferric iron-reducing bacteria (Lovely et al. 1996). Microorganisms more frequently reduce amorphous iron oxides than their crystalline forms and at neutral pH iron minerals are barely soluble (Straub et al. 2001). The Fe_o/Fe_d ratio indicates the degree of iron oxide crystallinity (McFadden and Hendricks 1985). The average value of the ratio Fe_o/Fe_d was higher for analyzed Rs. In general, higher values of this ratio are observed in soils rich in humic substances and soils developed under hydromorphic conditions (Schwertmann 1966; Jiang et al. 2011). The Fe_o component appears more important than organic carbon in terms of water-stable aggregates > 0.25 mm for soils with relatively low soil organic matter contents (Duiker et al. 2003). Amorphous iron in the form of poorly crystalline Fe oxide-hydroxides (e.g., ferrihydrite) is most often associated with clay minerals, and it occurs in the form of durable bonds with humus (Cornell and Schwertmann 1996). Clay minerals play an important role in aggregate stability of soils (Denef and Six 2005). Smectite

Table 3 Chemical properties of rhizospheric soil (Rs) and non-rhizospheric soil (nRs)

Samples	pH 1 M KCl	CaCO ₃ g kg ⁻¹	ECe dS m ⁻¹	Ca ²⁺ cmol ₍₊₎ kg ⁻¹	Mg ²⁺ kg ⁻¹	K ⁺	Na ⁺	TEB	TOC g kg ⁻¹	Nt	C:N	DOC mg kg ⁻¹	DOC in TOC %	Fe _o /Fe _d
Rs-1	7.17	5.0	0.33	18.1	0.9	0.4	0.1	19.5	24.6	2.5	9.8	876	3.6	0.59
Rs-2	7.17	6.8	0.62	29.3	2.4	0.2	0.1	32.0	23.6	2.3	10.3	656	2.8	0.48
Rs-3	7.03	4.5	0.54	34.7	2.4	0.2	0.1	37.4	30.4	2.8	10.8	671	2.2	0.60
Rs-4	6.96	4.5	0.51	23.3	2.1	0.2	0.4	26.0	32.7	3.1	10.5	889	2.7	0.47
Rs-5	6.84	4.0	0.75	42.5	1.3	0.2	0.1	44.1	48.1	4.6	10.4	1252	2.6	0.48
Rs-6	6.92	4.5	0.55	24.9	2.1	0.1	0.1	27.2	29.2	2.6	11.2	733	2.5	0.49
Rs-7	6.63	5.0	0.49	43.9	2.6	0.2	0.3	47.0	43.7	4.2	10.4	918	2.1	0.50
Rs-8	6.93	4.0	0.51	35.8	3.9	0.2	0.3	40.2	35.2	3.3	10.7	884	2.5	0.62
Rs-9	6.77	6.0	0.44	16.6	3.6	0.1	0.2	20.5	33.6	2.9	11.6	826	2.5	0.56
Rs-10	6.97	8.3	0.42	20.6	1.3	0.1	0.4	22.4	29.1	2.6	11.2	796	2.7	0.61
SD	0.17	1.38	0.11	9.86	0.97	0.09	0.13	10.03	7.77	0.75	0.53	169	0.41	0.06
CV (%)	2.4	26.3	21.2	34.0	42.2	45.0	65.0	31.7	23.6	24.2	5.0	19.9	15.8	11.2
nRs-1	7.03	8.1	0.27	16.6	0.7	0.2	0.5	18.0	24.1	2.1	11.5	804	3.3	0.54
nRs-2	7.08	8.2	0.29	23.3	2.4	0.5	1.3	27.5	21.4	2.3	9.3	676	3.2	0.44
nRs-3	7.11	11.7	0.31	35.5	2.3	0.6	0.8	39.2	27.2	2.9	9.4	790	2.9	0.53
nRs-4	6.68	5.5	0.23	22.3	2.1	0.3	1.2	25.9	27.8	3.0	9.3	725	2.6	0.52
nRs-5	6.93	6.9	0.34	38.5	2.3	0.3	0.7	41.8	28.9	2.8	10.3	730	2.5	0.53
nRs-6	6.74	0.0	0.25	24.3	1.6	0.3	0.6	26.8	23.1	2.5	9.2	612	2.6	0.48
nRs-7	6.81	11.0	0.51	36.3	2.4	1.0	0.8	40.5	39.1	3.3	11.8	860	2.2	0.30
nRs-8	6.63	6.4	0.36	32.3	1.9	0.6	0.8	35.6	30.7	3.0	10.2	663	2.2	0.37
nRs-9	6.66	8.0	0.39	13.6	1.6	0.7	0.9	16.8	21.7	1.6	13.6	661	3.0	0.39
nRs-10	6.81	8.3	0.26	17.3	0.9	0.4	1.8	20.4	27.6	2.5	11.0	848	3.1	0.33
SD	0.18	3.22	0.08	9.03	0.62	0.24	0.39	9.45	5.24	0.50	1.43	85.3	0.40	0.09
CV (%)	2.6	43.5	25.0	34.8	34.1	48.0	43.4	32.4	19.3	19.3	13.5	11.6	14.5	20.5

SD standard deviation, CV coefficient of variation, ECe electrical conductivity, TEB total exchangeable bases, TOC total organic carbon, Nt total nitrogen, DOC dissolved organic carbon, Fe_d free iron, Fe_o amorphous iron

is the predominant clay mineral both in analyzed Rs and nRs (Fig. 2). Smectite can be attracted to humic substances with exchangeable Ca²⁺ acting as bridges. Concentration of exchangeable Ca²⁺ in analyzed soil samples was relatively high as, after periodic flooding, the cations Ca²⁺ can be strongly bonded by negatively charged clay particles in fluvial deposits. Some studies indicated that increases in CEC are

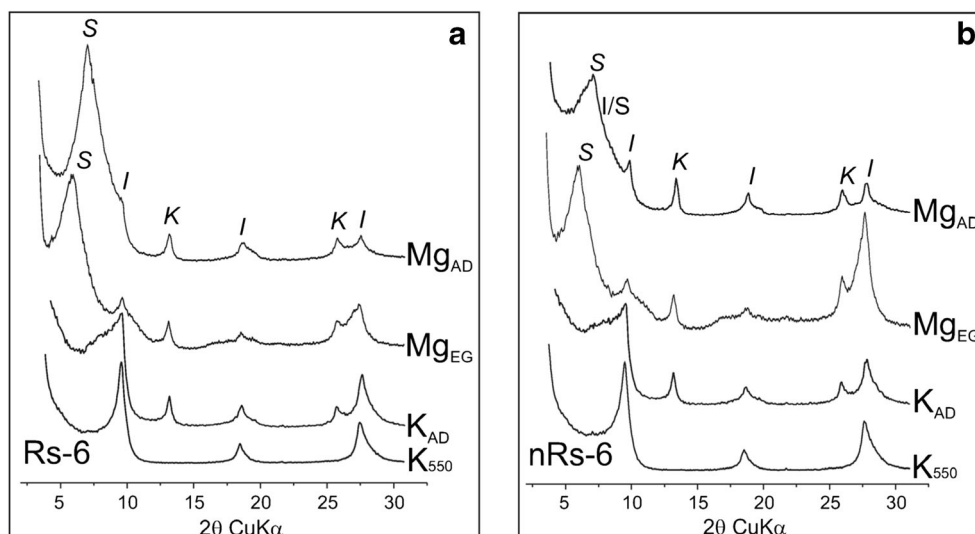
correlated with increasing reduction of structural Fe in smectite (Stucki et al. 1984). Reduction of structural Fe is associated with changes in chemical and physical features of clay minerals (Stucki 2011). Favre et al. (2002) found that after flooding, the cation exchange capacity of soils increased sometimes twice. Exchangeable Ca²⁺ improves soil structure through bridging with clay minerals and soil organic carbon (SOC). In analyzed soil materials, the humic acid-Ca-clay complexes are considered to be a reason for the development of water-resistant aggregates. Bronick and Lal (2005) found that clay-sized particles are commonly associated with aggregation by flocculation, although swelling clay minerals (smectites) can disrupt aggregates. Even though the expandability of smectites can disrupt aggregates during wet–dry cycles, still the aggregates in analyzed Rs showed a high resistance against disruption, similarly as aggregates in nRs. Aggregation is generally high in soils rich in smectites and other 2:1 clay minerals which are characterized by high CEC, large specific surface area, dispersivity, and expandability, which, in turn, affect SOC decomposition rates (Schulten and Leinweber 2000). Soils dominated by

Table 4 Correlation coefficient at *P* < 0.05 for selected properties

Properties	DOC	Fe _d	Fe _o	EE-GRSP
Rs (<i>n</i> = 10)				
Clay		0.60	0.65*	− 0.54
TOC	0.81*	0.50	0.35	0.54
DOC				0.77*
nRs (<i>n</i> = 10)				
Clay		0.62	0.71*	− 0.52
TOC	0.57	0.34		0.29
DOC				0.66*

*Significant value

Fig. 2 XRD patterns of clay fraction (<2.0 μm). **a** rhizospheric soil, **b** non-rhizospheric soil preparations of clay fraction: Mg_{AD} – Mg^{+2} -saturated air-dried, Mg_{EG} – Mg^{+2} -saturated and ethylene glycol-solvated, K_{AD} – K^{+} -saturated, K_{550} – K^{+} -saturated and heated at 550 °C. Clay minerals: *S* – smectite, *I* – illite, *I/S* – illite-smectite, *K* – kaolinite



kaolinite and other 1:1 clay minerals and oxides reveal a higher aggregation at lower SOC levels, whereas soils with mixed clays mineralogy show a higher aggregation at higher SOC (Denef et al. 2002).

Table 5 Result of spectrophotometric and chromatographic analyses of humic acids in rhizospheric soil (Rs) and non-rhizospheric soil (nRs)

Samples	A_{665}	A_{465}	$A_{4/6}$	HIL/HOB
Rs-1	0.82	5.01	6.11	2.97
Rs-2	0.74	4.73	6.39	2.39
Rs-3	0.75	4.89	6.52	2.79
Rs-4	0.81	5.64	6.96	2.69
Rs-5	0.91	6.34	6.97	2.25
Rs-6	0.74	4.71	6.36	2.32
Rs-7	0.65	4.20	6.46	2.21
Rs-8	0.83	5.34	6.43	2.06
Rs-9	0.67	4.14	6.18	1.91
Rs-10	0.65	4.28	6.58	2.52
SD	0.09	0.69	0.29	0.33
CV (%)	11.9	14.0	4.5	13.7
nRs-1	0.54	3.16	5.85	3.03
nRs-2	0.50	3.19	6.38	3.02
nRs-3	0.52	3.23	6.21	3.44
nRs-4	0.51	3.35	6.57	3.59
nRs-5	0.50	3.20	6.40	3.31
nRs-6	0.51	3.11	6.10	2.79
nRs-7	0.57	3.64	6.39	2.27
nRs-8	0.85	5.04	5.93	2.95
nRs-9	0.63	3.78	6.00	2.50
nRs-10	0.52	3.19	6.13	3.22
SD	0.11	0.59	0.33	0.41
CV (%)	19.7	16.9	5.3	13.7

Fractions of humic acids: hydrophilic (HIL) and hydrophobic (HOB)

The basic properties (texture, pH, $CaCO_3$, TOC, Nt, DOC, and exchangeable Ca^{2+} , Mg^{2+}) of Rs and nRs were similar. There were noted significant differences between Rs and nRs for exchangeable K^+ , Na^+ , ECe, A_{465} , A_{665} , HOB, HIL, EE-GRSP, Fe_d , Fe_c , and class of aggregates (7–5 and 5–3 mm) (Table 2). The content of TOC and DOC in the analyzed Rs was higher than in nRs. Organic carbon cycling is especially intensive in the rhizosphere, and it differs from root-free soil by a high amount of carbon that is easily available for microorganisms (Kuzyakov 2002).

The values of absorbance (Table 5), at wavelengths of 465 nm (A_{465}) and 665 nm (A_{665}), were significantly higher for HAs isolated from Rs than from nRs. The humification process advancement is determined by the value of absorbance $A_{4/6}$ ratio. The values of $A_{4/6}$ ratio were significantly higher for HAs isolated from Rs than HAs from nRs (Table 2). Higher values of $A_{4/6}$ ratio obtained for analyzed HAs of Rs reflect a

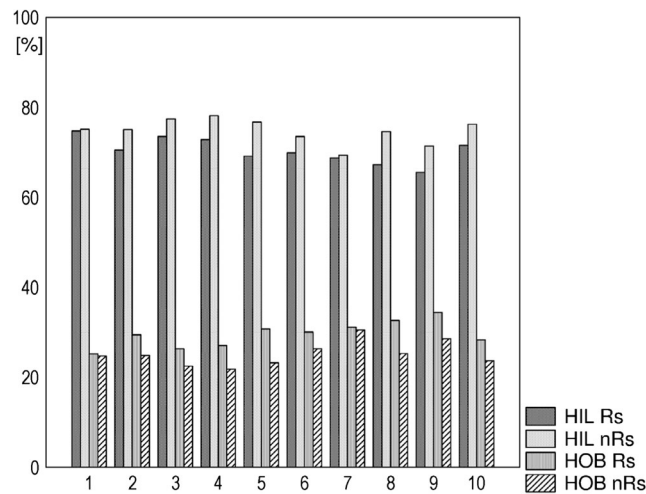


Fig. 3 Hydrophilic (HIL) and hydrophobic (HOB) fractions of humic acids in rhizospheric soil (Rs) and non-rhizospheric soil (nRs)

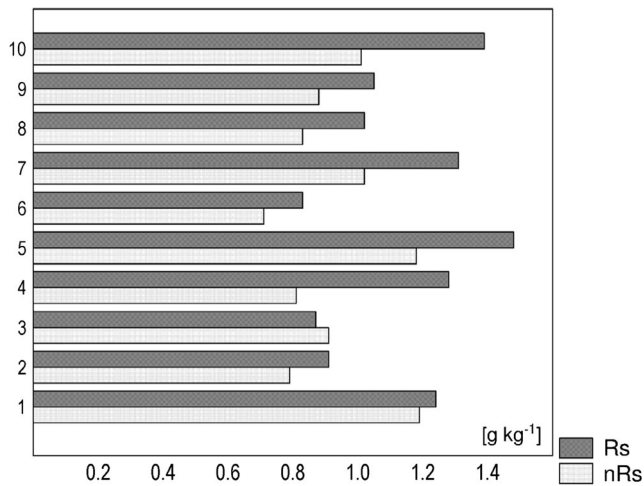


Fig. 4 Content of glomalin (EE-GRSP) in rhizospheric soil (Rs) and non-rhizospheric soil (nRs)

higher content of humic substances at the initial decomposition stage as compared with the HAs of nRs. Vieyra et al. (2009) indicated that the value of $A_{4/6}$ ratio is higher for non-humified material by the presence of proteins and carbohydrates. A high value of $A_{4/6}$ ratio reflects a low degree of condensation of aromatic compounds (Chen et al. 1977; Albrecht et al. 2011). This ratio is also inversely related to the particle size and molecular weight of HAs (Uyguner et al. 2004). Respective humic substances differ in their degree of polymerization of the aromatic nucleus, the kind, and the number of functional groups, which affects the nature and the strength of bonds with mineral soil components. Humic substances with a lower molecular weight are a more labile SOM fraction (Neff and Asner 2001; Marinari et al. 2010). The results of the spectrometric analysis of analyzed HAs were also consistent with a higher average DOC content in Rs compared to nRs.

A higher share of HOB fractions, seen from lower values of the HIL/HOB ratio, points to the presence of HAs showing a higher degree of aliphaticity, a lower molecular weight, and the presence of simple aromatic structures (Dębska et al. 2010, 2012). Both the share of HIL and

Table 6 Soil aggregate stability SAS [%]

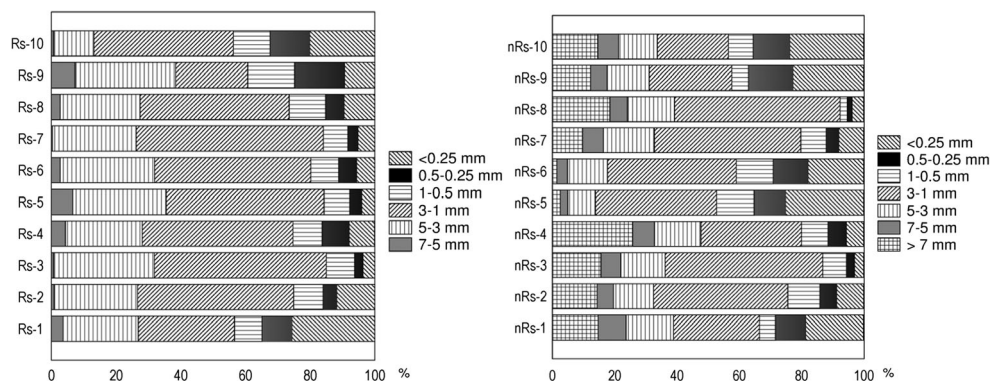
Samples	Class of aggregates [mm]					
	>7	7–5	5–3	3–1	1–0.5	0.5–0.25
Rs-1	–	98.6	97.7	94.3	91.7	83.9
Rs-2	–	99.1	98.9	95.0	91.8	90.8
Rs-3	–	98.0	98.9	95.7	94.3	90.6
Rs-4	–	99.4	99.4	97.7	94.5	94.2
Rs-5	–	98.7	99.2	98.6	91.7	86.6
Rs-6	–	99.2	99.4	99.2	95.9	96.8
Rs-7	–	99.5	99.6	99.3	96.2	97.5
Rs-8	–	98.4	98.8	95.8	91.8	91.5
Rs-9	–	96.1	89.1	86.6	89.0	93.0
Rs-10	–	99.9	99.5	97.6	95.7	95.9
SD	–	1.07	3.19	3.73	2.39	4.38
CV (%)	–	1.1	3.2	3.9	2.6	4.8
nRs-1	99.2	98.3	98.8	97.9	95.7	81.2
nRs-2	98.6	98.1	98.5	94.4	89.7	93.6
nRs-3	99.6	99.0	97.8	96.6	92.5	94.9
nRs-4	71.4	94.6	93.2	92.6	92.3	93.5
nRs-5	99.6	98.5	98.8	96.3	93.7	86.4
nRs-6	99.6	98.9	99.1	98.0	96.9	96.1
nRs-7	99.7	99.7	99.4	98.5	98.1	96.2
nRs-8	99.7	97.5	97.6	96.5	92.8	87.2
nRs-9	95.5	78.6	77.6	78.4	77.6	51.3
nRs-10	99.8	99.3	99.4	97.2	96.8	96.5
SD	8.83	6.36	6.72	5.97	5.87	13.78
CV (%)	9.2	6.6	7.1	6.3	6.3	15.7

SD standard deviation, CV coefficient of variation

HOB fractions as the value of the HIL/HOB ratio show that the HAs isolated from analyzed Rs demonstrated a slightly higher content of humic substances at the initial decomposition stage, as compared with the nRs.

Humic substances are key components of soil aggregates, and, with complex carbohydrates synthesized by bacteria, they function together with clay fraction to form soil

Fig. 5 Classes of aggregates in rhizospheric soil (Rs) and non-rhizospheric soil (nRs)



aggregates (Spohn and Giani 2010). Plant roots and their rhizosphere zone have many effects on soil aggregation with increasing root length density, microbial activity, and content of glomalin (Rillig et al. 2002). Concentration of glomalin-related protein (GRSP) in soil is positively correlated with aggregate water stability (Rillig 2004). Analyzed Rs, adjacent to the roots of common dandelion, contained a significantly higher EE-GRSP concentration than nRs (Fig. 4). The concentration of glomalin from arable soils, grasslands, and natural ecosystems is, on average, 2 g kg^{-1} to 15 g kg^{-1} (Wright and Upadhyaya 1996; Wright et al. 2000); however, it was observed that its amount decreases due to frequent agrotechnical treatments (Wright et al. 1999; Preger et al. 2007). Wright et al. (2007) showed differences in GRSP concentration in different soil size-fractions due to soil management. In analyzed soil materials, the concentration of EE-GRSP and the content of DOC were closely correlated both in Rs and nRs (Table 4). The obtained results confirm the observations of other researchers that soil organic carbon is related to glomalin concentration (Nichols and Wright 2005; Schindler et al. 2007; Šimanský et al. 2013). Arbuscular mycorrhizal fungi produce glomalin-related protein, even though this activity seems to be controlled by soil texture (Wright et al. 2007). As a result, the concentration of EE-GRSP was negatively but non-significantly correlated with the content of clay fraction both in analyzed Rs and in nRs (Table 4).

The analyzed class of aggregates (7–0.25 mm) demonstrated a very high resistance against disruption when exposed to water. The difference was non-significant; however, in comparison with nRs, the rhizospheric aggregates were characterized by higher mean values of SAS (Table 2).

5 Conclusions

The physical and chemical properties, determining the current soil aggregates stability, must be comprehensively interpreted due to their interactions and intricate feedback mechanisms. A very high stability of aggregates was identified, both in Rs and nRs, even though they differed significantly in the content of exchangeable K^+ , Na^+ and ECe , Fe_d , Fe_o , and the concentration of EE-GRSP. The Rs as well as nRs contained high amounts of exchangeable Ca^{2+} , and smectite was the predominant clay mineral. It exerted positive effect on the accumulation of organic carbon and the formation of soil with good tilth. Besides, the dominance of smectite in clay fraction both in Rs and in nRs did not result in a decrease in the soil aggregate stability. With that in mind, one can conclude that higher SAS values for the Rs, despite a lower content of the iron forms studied, point to the dominant role of soil organic matter in forming stable aggregates.

The HAs isolated from Rs revealed a significantly higher content of humic substance at its initial phases of decomposition, as compared with nRs. A higher share of HOB fractions, corresponding to a lower value of HIL/HOB ratio, points to the presence of HAs in Rs with a greater aliphaticity, a lower molecular weight and a presence of simple aromatic structures.

The mycorrhizal hyphae of common dandelion contributed to improved soil aggregation by the production of glycoprotein which may act as a cementing agent for soil particles. The highest mean contribution of 1–3-mm soil aggregates was recorded in Rs as well as in nRs. Despite a similar particle-size distribution of nRs and Rs, higher SAS values of the rhizospheric soil were affected by TOC, DOC, the concentration of exchangeable Ca^{2+} and EE-GRSP, and, less considerably, the content of Fe_d , Fe_o , and the composition of clay minerals. A variation in those parameters and slight differences in the texture and the content of TOC, on the other hand, resulted in Rs containing significantly more aggregates 5–3 mm in diameter.

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