Humus Quality in Hydromorphic Soils of the Island of Rab

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Summary

The aim of the study was to determine humus quality in hydromorphic soils of the island of Rab. The study was conducted on 16 samples collected from the anthropogenic top-soil horizon in which were determined total organic carbon according to Walkley-Black method (1934) and fractional composition of humic substances following the procedure given by Schnitzer (1982) using 0.1 M NaOH and 0.1 M $Na_4P_2O_7$ as extraction solution. Spectroscopic characterization of isolated humic substances was carried out by measuring absorbance in VIS spectral range of 400-700 nm and optical indices ($Q_{4/6}$, $E_{4/6}$) were calculated. Investigated soils had sandy silty loam texture, acidic to alkaline pH, low content of physiologically active phosphorus and potassium, hydroameliorated by channels and were used as pastures. The total organic carbon content was low (0.95% in average) and varied from 0.42 to 1.86%. The average C/N ratio was 12.7. The humic acid content varied from 0.09 to 0.38% and fulvic acid content varied from 0.10 to 0.55%. The humification degree was low to medium, in average 21.5%. The average HA/FA ratio was 0.84 that indicated the domination of fulvic-humic type of isolated humic substances. The average optical indices $Q_{4/6}$ and $E_{4/6}$ were 5.92 and 5.62, respectively, which corresponded to the presence of more aliphatic and fewer aromatic compounds. The obtained results indicated low humus quality of investigated hydromorphic soils.

Key words

humic substances, humic acid, fulvic acid, humification degree, optical indices

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Introduction

Humus defines key soil characteristics and its fertility, and it is an indicator of the processes in soil. Therefore, understanding of its content and quality is important for the sustainable management of agricultural land. Although there is a great interest in the role of humus in ecosystem function, there have been few studies providing unequivocal identification and quantification of humus because of the heterogeneous and polydisperse nature of humic substances, and the complexity of the inter- and intramolecular reactions (Yang et al., 2002). Humic substances (HS) constitute a major fraction (60–70%) of soil organic matter and are possibly the most abundant of naturally occuring organic macromolecules on the earth (2–3 x 10^{10} t), (Jones and Bryan, 1998).

The classical method of fractionation of HS is based on differences in solubility in aqueous solutions at widely differing pH levels (Kononova, 1966). Bruckert (1979) distinguished several types of extraction solution. Alkali extraction is able to destroy the most organomineral bonds and have been widely used for recovering organic matter. The extraction with 0.1 or 0.5 M NaOH leads to the recovery of approximately two-thirds of the soil organic matter. In this paper we used method of Schnitzer (1982) with a mixture of 0.1 M NaOH and 0.1 M $Na_4P_2O_7$ as the extractant because of its successfulness in maximizing extraction of humic compounds and minimizing their degradation with yield comparable results. Also, it is suitable for all types of soil and there is no need for pretreatment with hydrochloric acid even in calcareous soil.

To determine humic substances chemical properties, as for the structure determination, non-destructive spectroscopic methods are commonly used. They are more convenient compared with the classical methods of fractionation, which are tedious and laborious, and not suitable for large number of samples. Therefore new approaches of spectrometry that include a wide variety of techniques (UV–VIS, DRIFT, SFS, and ^{13}C-NMR) have been successfully applied to the study of HS chemical composition and structure (Pospišilova et al., 2008; Milori et al., 2002; Sierra et al., 2005). Humic substances generally show strong absorbance in the UV–VIS range (from 190 to 700 nm), because of the presence of aromatic chromophores and other organic compounds (Schnitzer and Khan, 1972). Ultraviolet-visible spectra of humic substances according to Orlov (1985) and Kumada (1987) and calculated optical indices ($E_4/_6$ and $Q_{4/6}$) are able to characterize satisfactorily the HS quality, maturity, and condensation degree. $E_4/_6$ ratio for humic substances in aquaeous solution correlates negatively with increasing content of condensed aromatic structures (Bravard and Righi, 1991; Stevenson, 1994). The best method for measuring degree of humification is still being debated because there is no well-defined model of humic substances structure. Therefore, humification degree is usually evaluated through indirect measurements that reflect the structural changes that occur during the humification process.

There are many various methods for assessing the quality of humus based on different principles. Determination of the total organic carbon and nitrogen using methods of elementary analysis and determination of C/N ratio belong to standard procedures. For assessing the quality of humus the ratio is often used of the absorption of pyrophosphate soil extract at 465 nm and 665 nm (A_{465}/A_{665}) because there is a significant correlation between the ratio of absorbances and the ratio of the content of humic and fulvic acids (HA/FA) (Sparks, 1996). Another commonly used method is the fractionation of humus compounds based on the various solubility of humic acids, fulvic acids and other humus substances at various pH (Guerra and Santos, 1999). The most frequently is used a combination of standard methods (C/N ratio, HA/FA ratio, degree of condensation of HS) and optical properties of alkaline extracts of humus substances (Duffkova et al., 2005).

The objectives of this study were to determine humus composition and to evaluate its quality in hydromorphic soils of the Adriatic island of Rab.

Materials and methods

The study was conducted on 16 soil samples taken from anthropogenic top-soil horizon (0-30 cm) of hydromorphic soils from island of Rab during 2013.

Basic soil properties

The samples were air-dried, passed through a 2 mm sieve, and analysed for their physical and chemical properties using conventional methods (HRN ISO 11464:2009). In particular: (a) soil pH was measured using a combined glass electrode in a 1:5 (*v/v*) suspension of soil in water and soil in 1 M KCl solution (HRN ISO 10390:2005); b) soil organic carbon was determined according to Walkley-Black method (1934); c) total nitrogen by modified Kjeldahl method (HRN ISO 11261:1995); d) available phosphorus and potassium were determined according to Egner-Riehm-Domingo with ammonium lactate-acetate as the extraction soultion (Egner et al., 1960); e) carbonate content was determined by modified volumetric method (HRN ISO 10693:1995); f) physiologically active lime according to Drouineau-Galet (JDPZ, 1966); g) particle size distribution was made by sieving and sedimentation using 0.1M Na-metaphosphate solution as dispersant (HRN ISO 11277:2009).

Humic substances

The isolation of soil humic substances (HS) was made by Schnitzer method (1982). 5 g of air dried soil sample was sieved at the mesh size of 1 mm and extracted with solution of 0.1 M NaOH + 0.1 M $Na_4P_2O_7$. The mixture was shaken mechanically for 24 h at room temperature. The supernatant solution was then separated from the residue by centrifugation at 4000 rpm for 20 min. The alkaline extract was acidified with concentrated H_2SO_4 to pH~1, allowed to stand for 24 h at room temperature to obtain the complete precipitation of humic acid (HA). The precipitated HA was separated from fulvic acid (FA) by repeating three times the following: centrifugation at 4000 rpm for 20 min, removal of the residue, and washing the HA with 0.05 M H_2SO_4 solution. Finally, the centrifuged HA were dissolved in a minimal volume of 0.1 M NaOH and brought to dryness in a drying oven at 60°C. Sum of HS, HA and FA were determined by titrimetric method in aliquot volumes.

Spectral characterization

VIS spectra were measured by Shimadzu UV 1700 spectrometer in the range of 400-700 nm. The extracts were prepared as a mixture of 0.1 M NaOH and 0.1 M $Na_4P_2O_7 \times 10\ H_2O$. Optical

Table 1. Statistical parameters for chemical soil properties

Stat.	pH (1:5)		$CaCO_3$	CaO	P_2O_5	K_2O
	H_2O	1 M KCl	%	%	mg/100 g of soil	
Mean	7.65	6.94	3.58	0.69	14.11	6.65
Minimum	6.74	5.32	0.00	0.00	5.00	1.90
Maximum	8.47	7.63	11.10	3.00	22.00	12.00
Coef. Var.	6.63	10.02	119.63	159.06	29.95	44.39

Table 2. Statistical parameters for soil particle size distribution

Stat.	Texture classes (%)				
	Coarse sand 2.0-0.2 mm	Fine sand 0.2-0.063 mm	Coarse silt 0.063-0.02 mm	Fine silt 0.02-0.002 mm	Clay < 0.002 mm
Mean	6.65	35.90	30.14	15.73	11.58
Minimum	1.90	19.00	17.20	7.00	5.30
Maximum	12.00	50.00	44.00	25.40	22.90
Coef. Var.	44.39	26.38	22.46	35.35	44.86

Table 3. Statistical parameters for soil organic carbon (SOC), nitrogen (N), C/N ratio, humic acid (HA), fulvic acid (FA), HA/FA, humification degree (HD) and optical indices $E_{4/6}$ and $Q_{4/6}$

Stat.	SOC	N	C/N	Fractional composition of humic substances			HD	Optical indices	
	%	%		HA %	FA %	HA/FA	%	$E_{4/6}$	$Q_{4/6}$
Mean	0.95	0.10	12.66	0.20	0.25	0.84	21.54	5.62	5.92
Minimum	0.42	0.05	5.60	0.09	0.10	0.40	15.30	4.66	4.38
Maximum	1.86	0.15	23.40	0.38	0.55	1.10	33.60	7.39	7.25
Coef. Var.	40.33	34.40	55.13	35.05	52.79	23.29	19.91	13.72	13.66

indices $E_{4/6}$ and $Q_{4/6}$ were determined as the absorbance ratio A_{465}/A_{665} and A_{400}/A_{600}, respectively (Orlov, 1985; Szajdak et al., 2006). Humification degree was calculated as a sum of humic acids /SOC×100 according to Orlov (1985).

Results and discussion

According to the national soil classification in Croatia (Škorić et al., 1985), these soils belong to hydromorphic soil order, anthropogenic soils class, hydroameliorated soil type formed on the eolian sands mixed with flysch drifts. Investigated soils are used as pastures, previously used as arable land.

Basic soil properties

Analyzed soils show acidic to alkaline reaction, neutral in average (Table 1). Soils are non-carbonate to slighty carbonate, with very low content of active lime. Available phosphorus content varies in wide range, while the mean value of P_2O_5 indicates low supply of soil with physiologically active phosphorus. Available potassium content is medium.

Analyzed soils have sandy loam to loam texture, predominantly sandy silty loam (Table 2). Great variability of $CaCO_3$ and CaO content (Table 1) and texture (Table 2) is the result of variations in the share of flysch drift and eolian sands.

The soil organic carbon (SOC) is very low to low (<1%, Table 3). Around 45% of the mineral soils in Europe have very low (<1%) and low (1-2 %) SOC (Rusco et al., 2001), and 74% of the land in southern Europe is covered by soils that have less than 2% SOC in the topsoil (Zdruli et al., 2007). In Mediterranean areas, where some soils have been cultivated for more than 2000 years, low level and the decline in natural content of organic matter may be much larger (Rusco et al., 2001). Analyzed soils are poorly to well-stocked with total nitrogen and C/N ratio varies in wide range, with average value 12.7 (Table 3). C/N ratio wider than 10 indicates lower humus quality (Prax et al., 1995).

Humic substances composition

The humic acids (HA) content varies from 0.09 to 0.38% and fulvic acid (FA) content varies from 0.10 to 0.55% (Table 3). The average HA/FA ratio is 0.84, which indicates a low level of humification and the domination of fulvic-humic type of isolated humic substances. Similar HA/FA ratios in surface horizons of hydromorphic soil were determined by Grubišić and Hojka (2003) and Dugonjić et al. (2013).

The humification degree (HD) of humic substances is low to medium; medium in average (21.5%), (Table 3.) Similar values of humification degree of humic substances in hydromorphics

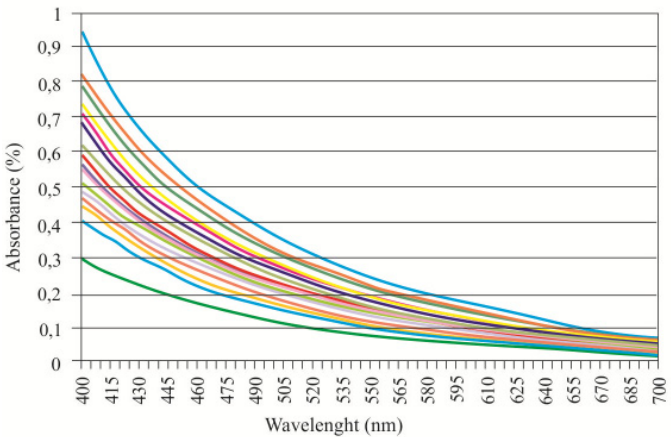

Figure 1. VIS spectra of extracted soil humic substances (HS) from top-soil horizon

soil were determined by Pospišilova and Fasurova (2009) and Pospišilova et al. (2010).

VIS spectroscopic characterization of humic substances

Spectrophotometry is one of the most widely applied methods used to evaluate the qualitative characteristics of organic matter (Brown, 1980; MacCharty and Rice, 1985). The absorption spectrum of the humic substances (HS) extracted from the studied soils shows monotonic decrease of absorbance in the range 400-700 nm (Figure 1).

The composition of organic matter and evaluation of humification degree are frequently characterized by determining the ratio between the absorbance at 465 nm and 665 nm ($E_{4/6}$) and the $Q_{4/6}$ (A_{400} nm/A_{600} nm). Generally, lower molecular weight and lower degree of condensation of aromatic structures show higher values of $E_{4/6}$ and $Q_{4/6}$ than humic substances with a high degree of humification (Orlov, 1985). These ratios have been reported to be independent of concentrations of humic materials but to vary for humic materials extracted from different soil types (Kumada, 1987). The optical indices ($E_{4/6}$ and $Q_{4/6}$) of humic substances of investigated soils in this study vary in the range 4.66-7.39, average 5.62 and 4.38-7.25, average 5.92, respectively (Table 3). High $E_{4/6}$ and $Q_{4/6}$ indices (> 4) indicate the presence of more aliphatic and fewer aromatic compounds and low humus quality. This results are in agreement with previous study of humic substances quality on similar hydromorphic soils, which also determined low humus quality (Pospišilova and Fasurova, 2009; Pospišilova et al., 2010; Hudec and Hegedusova, 2013).

The results of the characterization of the HS using classical chemical analysis (C/N, HA, FA, HA/FA and HD) and VIS spectroscopy are basically in agreement with each other. Average C/N ratio wider than 10, HA/FA ratio below 1 and optical indices ($E_{4/6}$ and $Q_{4/6}$) above 4 indicate low quality of humus in investigated soils.

Conclusion

The soil organic carbon content (SOC) of investigated soils is very low to low. Isolated humic substances (HS) are fulvic-humic type. Average C/N ratio 12.7 and HA/FA ratio 0.84, as well as humification degree 21.5 indicate dominantly low humus quality. VIS spectroscopically established optical indices ($E_{4/6}$ and $Q_{4/6}$) above 4 indicate the presence of more aliphatic and fewer aromatic compounds and confirm results of classical chemical analysis.

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