

## TOTAL CARBON CONTENT AND HUMIC SUBSTANCES QUALITY IN SELECTED SUBTYPES OF CAMBISOLS

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### Abstract

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Cambisols cover an estimated 45% of agricultural soils in the Czech Republic. We aimed our work at stabile forms of organic carbon and humic substances quality in Cambisols under different types of soil management (grassland and arable soil). Object of our study were the following subtypes of Cambisols: Eutric Cambisol (locality Vatin – arable soil), Eutric Cambisol (locality Vatin – grassland), Haplic Cambisol (locality Náměšť n/Oslavou – arable soil), Leptic Cambisol (locality Ocmanice – grassland), Haplic Cambisol (locality Nové Město na Moravě – arable soil), Haplic Cambisol (locality Přemyslov – Tři Kameny – grassland), Arenic Cambisol (locality Pocoucov – arable soil), Dystric Cambisol (locality Sněžné – arable soil), Dystric Cambisol (locality Velká Skrovnice – arable soil), Dystric Cambisol (locality Vojnův Městec – arable soil). Non-destructive spectroscopic methods such as UV-VIS spectroscopy, synchronous fluorescence spectroscopy (SFS) and  $^{13}\text{C}$  NMR spectroscopy for humic substances (HS) quality assessment were used. Total organic carbon (TOC) content was determined by oxidimetric titration. Fractionation of HS was made by short fractionation method. Isolation of pure humic acids (HA) preparation was made according to the standard IHSS method.

Results showed that TOC and humus content varied from 2.70 % (grassland) to 1.3 % (arable soil). Average HS sum was 8.4 mg/kg in grassland and 6.4 mg/kg in arable soil. Average HA sum was 3.6 mg/kg in grassland and 3 mg/kg in arable soil. Fulvic acids (FA) content was 4.7 mg/kg in grassland and 3.7 mg/kg in arable soil. HS quality was low and very similar for all studied samples. HA/FA ratio low ( $< 1$ ). HS absorbance in UV-VIS spectral range was low and similar in all studied samples. Higher absorption in this spectral range was closely connected with higher HS content. Also in 2D-synchronous fluorescence scan spectra similar shape of spectral lines was detected. Relative fluorescence intensity strongly depended on HA and FA content. Five main fluorescence peaks for HA and FA presence at  $\lambda_{\text{ex.}}/\lambda_{\text{em.}}$ : 468/488, 482/502, 450/470, 376/396, 340/360 at constant difference of  $\Delta\lambda=20$  nm were measured.  $^{13}\text{C}$  NMR spectra of HA isolated from Eutric Cambisol showed low aromaticity degree and high content of aliphatic moieties. HA were young (= less aromatic compounds in HA molecule) and no differences in HA structure were detected to compare arable soil and grassland.

humus fractionation, UV-VIS, SFS and  $^{13}\text{C}$  NMR spectroscopy, Cambisols

Cambisols combine soils with at least an incipient subsurface soil formation. Transformation of parent material is evident from structure formation and mostly brownish discoloration, increasing clay percentage, and carbonate removal. Dynamic of soil carbon storage and release in this soil type is still poorly understood. Hayes et al. (1990) have summarized the role of organic matter in soils as follows: 1. formation and maintenance of a good structure; 2. im-

provement of water capacity; 3. retention in available form of plant nutrients by cation-exchange processes; 4. slow release of nitrogen, sulphur, phosphorus and some trace elements; 5. transport of metals into plant roots; 6. stimulation of plant growth; 7. immobilization of some anthropogenic chemicals added to the soil; 8. soil buffering capacity enhancement; 9. raising the soil temperature. The agronomic functions of the organic matter through its effect on

the physical, chemical and biological properties of the soil directly involve environment itself. For these reasons it is important to be able to assess the presence and quality of soil organic matter (SOM) that reach soil. In general, soil organic carbon could be divided into two groups – stabile and labile organic carbon forms. Stabile forms of organic carbon are represented by total carbon content (TOC), humic substances (HS) sum, humic acids (HA) sum and fulvic acids (FA) sum. Labile forms are represented by dissolved organic carbon.

The best analytical method for extraction, isolation and complete HS characterization is still being discussed. HS differ in molecular weight, elemental composition, acidity and cation exchange capacity. The humic acids fraction consist of hydroxyphenols, hydroxybenzoic acids, and others aromatic structures with linked peptides, amino compounds, and fatty acids. Fulvic acids are typically composed of a variety of phenolic and benzene carboxylic acids. Fulvic acid molecule held together by hydrogen bonds to form stable polymeric structures or by association with polysaccharides. The last also contain more oxygen, less carbon and more acidic functional groups, particularly – COOH to compare with HA. A difficulty with HS chemical extraction is that they are tedious and labor intensive and not suitable for large numbers of samples. New approaches of spectrometry that include a wide variety of the spectroscopic techniques have been successfully applied (Peauvouri et al., 2002). Hayes (1985) and Stevenson (1982) showed that absorbance at wavelength 465 nm is equal to light absorption of components associated with the first phases of humification process (young humic substances). Light absorption at 665 nm is related to well humified components. Low  $Q_{4/6}$  values ( $< 4$ ) indicate high HS quality, which is known by Chernozems, usually. So that UV-VIS spectral lines and indexes ( $Q_{4/6}$ ) are frequently used for characterization HS quality, maturity and condensation degree.

Synchronous fluorescence spectra (SFS) performed the high resolution of spectral peaks. Miano and Senesi (1992) reported that the most efficient fluorophores are indicated to be variously substituted, condensed aromatic rings, and/or highly unsaturated aliphatic chains. Peuravuori et al. (2002) divided fluorescence spectrum into several regions according to certain wavelengths and assumed that certain polycyclic contributors are responsible for humic fluorescence properties. Humic substances fluorescence spectroscopy is a sensitive method, with concentration interval in range from 1 to 100 mg/l at different spectrofluorimeters. Number of major fluorescence peaks is equal to number of present fluorophores in humic structure. Fluorescence spectroscopy can also diversify the presence of HA or FA, via SFS measurements. Short wavelengths of major fluorescence peaks are typical for FA and long wavelengths for HA. Some of UV-VIS and SFS spectra of Czech soil humic acids samples

were also considered by Pospíšilová et al. (2005, 2006, 2008).

$^{13}\text{C}$  – Nuclear Magnetic Resonance (NMR) is often used for the elucidation of organic compounds and mixtures structure. We receive a specific piece of information on the chemical structures involving  $^{13}\text{C}$  atoms within a molecule. The carbon skeleton of HS is observed rather than the adjacent protons, allowing the functional groups to be detected. Carbon nuclei are spread over a wide range of chemical shifts that effectively separate signals even when carbons have only small differences in diverse structural environments (Simpson, 2002). Carbon structures are determined in relative terms from the chemical shifts that occur when energy is absorbed by a molecular spinning in a magnetic field. Individual carbon types in molecule indicate structure, sorption capacity, binding properties and solution interactions of HS (Wilson, 1987 and Simpson, 2002). However, NMR analysis is not always accessible because it is very complex and expensive technique.

We focused our work on stabile carbon forms in the soil. HS were isolated from selected subtypes of Cambisols and their quality was studied using non-destructive spectroscopic techniques including UV-VIS, SFS and  $^{13}\text{C}$  NMR spectroscopy.

## MATERIAL AND METHODS

Soil samples were collected from the top soil and following subtypes of Cambisols were studied: Eutric Cambisol (locality Vatin – arable soil), Eutric Cambisol (locality Vatin – grassland), Haplic Cambisol (locality Náměšť n/Oslavou – arable soil), Lepitic Cambisol (locality Ocmanice – grassland), Haplic Cambisol (locality Nové Město na Moravě – arable soil), Haplic Cambisol (locality Přemyslov – Tři Kameny – grassland), Arenic Cambisol (locality Pocoucov – arable soil), Dystric Cambisol (locality Sněžné – arable soil), Dystric Cambisol (locality Velká Skrovnice – arable soil), Dystric Cambisol (locality Vojnův Městec – arable soil). Basic characteristics of studied subtypes are listed in Tab. I.

Soil reaction was determined by potentiometric method. Texture was determined by pipette method. We analysed TOC content by oxidimetric method according to Nelson and Sommers (1982). Fractional composition of HS was determined as follows: 5g of air-dried soil sample sieved at mesh size of 1mm and extracted by a mixture (1:1, 0.1M NaOH + 0.1M  $\text{Na}_4\text{P}_2\text{O}_7$ ) for 24h. The sediment was separated by centrifugation at 2800g for 10min, washed with mixture and centrifuge again. Two individual washings were unified with original supernatant, acidified with concentrated  $\text{H}_2\text{SO}_4$  to pH 1.5. We allowed to precipitate HA overnight. TOC content was estimated by titrimetric method in aliquot volumes (Podlešáková et al., 1992).

Isolation of soil HA was made according to the standard international IHSS method (Hayes, 1985). 100g of air-dried soil sample, sieved at mesh size of 1mm, washed by 10 % HCl and stirred for 1–2

hours (decalcination process). After negative reaction for  $\text{CO}_2$  (detected by seeing no  $\text{CO}_2$ ), the soil rest was washed by 0.05 M HCl. After negative reaction for  $\text{Ca}^{2+}$  (detected by ammonium oxalate), the soil rest was washed by distilled water. After negative reaction for  $\text{Cl}^-$  (detected by  $\text{AgNO}_3$ ), the soil rest was shaken in a 0.1 M NaOH for 7–8 hours. We allowed it to precipitate over night and then centrifuge 15 minutes at 5000 rpm. Elution with 0.1 M NaOH and centrifugation was followed two times and supernatant solutions were mixed. Dark-brown solution of HS was precipitated by concentrated HCl to pH = 1. The coagulated HA were decanted, washed several times, extensively purified by 0.5% mixture HCl+HF and dialyzed against distilled water until chloride-free, and freeze-dried.

UV-VIS spectra were measured in mixture 0.1 M pyrophosphate sodium and 0.1 M NaOH. We used UV-VIS spectrometer Cary Probe 50 Varian with optical fibre within the range 300–700 nm.

SFS scan spectra were measured (after filtration and appropriate dilution) within the range 300–600 nm using spectrofluorimeter Aminco Bowman Series 2 (Thermospectronics, Xe-lamp, scan sensitivity 60%, autorange 845 V, bandpass of both monochromators 4 nm, relative fluorescence intensity 0–9.99, 2D scan mode, temperature 20°C and the constant difference was  $(\Delta\lambda_{\text{em.}} - \Delta\lambda_{\text{ex.}}) = 20$  nm between both excitation and emission monochromators). Synchronous fluorescence scan (SFS) is used for the measurement when a constant difference  $\Delta\lambda = (\lambda_{\text{em.}} - \lambda_{\text{ex.}})$  between both monochromators is set. For SFS spectral record was plot in two modes: on x-axis is excitation wavelength (Synchronous-scan excitation fluorescence spectra), or emission wavelength, usually. All spectral lines were measured in the mixture of 0.1 M pyrophosphate sodium solution and 0.1 M NaOH. Measurements were kindly made at Brno University of Technology, Institute of Physical and Applied Chemistry.

$^{13}\text{C}$  Nuclear Magnetic Resonance (NMR) was carried out on spectrometer Varian INOVA 600 (frequency 150,830 MHz). For NMR experiments 100 mg of isolated HA samples were dissolved in 2.5 ml of 0.5 M NaOH in deuterated water. After 24 hour of intensive stirring 0.5 ml of HA sample was put in 5 mm NMR cell. All  $^{13}\text{C}$  NMR experiments were run at 23°C on a Varian Unity – INOVA 600 MHz spectrometer using basic one-pulse experiment with the following set of the acquisition parameters: spectrometer frequency 242.803 MHz; relaxation delay 1 s, acquisition time 1.6 s; excitation pulse flip angle 45°, spectral width 50000 Hz and a continuous broadband decoupling of the protons. Prior Fourier transformation accumulated data were fitted with exponential function (line broadening 10 Hz). Subdivision of the spectrum was made by the commonly used scheme on Malcolm (1990). Aromatic carbon ( $\text{C}_{\text{ar}}$  %) is represented in the  $\delta$  106–157 ppm spectral region. Aliphatic carbon ( $\text{C}_{\text{aliph}}$  %) is represented in the  $\delta$  15–106 ppm spectral region. Aromaticity degree of HA ( $\delta$ ) was calculated

according to Hatcher et al. (1981).  $^{13}\text{C}$  NMR spectra were kindly measured at Slovak University of Technology, Faculty of Chemical and Food technology, Department of NMR Spectroscopy and Mass Spectroscopy in Bratislava.

## RESULTS AND DISCUSSIONS

Cambisols, although less fertile, are used intensively for mixed farming, grazing and as forest land. Studied subtypes of Cambisols occur in places higher than 400 m.a.s.l. Studied soils were silty clay textured and their acidity was high – see Tab. I. Humus content was low and varied from 2.7% to 1.3% in grassy soil and arable soil, respectively (Fig. 1). Maximum was 2.7% TOC in Haplic Cambisol (Přemyslov – Tři Kameny, grassland). Minimum was 1.3% TOC in Haplic Cambisol (Náměšť n/Oslavou, arable soil) – see Tab. II. Average HS sum was 8.4 mg/kg in grassland and 6.4 mg/kg in arable soil. Maximum HS content was 11 mg/kg in Haplic Cambisol (Přemyslov – Tři Kameny, grassland). Minimum HS content was 4 mg/kg in Arenic Cambisol (Pocoucov, arable soil). Average HA sum was 3.6 mg/kg in grassland and 3 mg/kg in arable soil. Maximum HA content was 4.3 mg/kg in Haplic Cambisol (Přemyslov – Tři Kameny, grassland). Minimum HA content was 1.5 mg/kg in Arenic Cambisol (Pocoucov, arable soil). Fulvic acids (FA) content was 4.7 mg/kg in grassland and 3.7 mg/kg in arable soil. FA maximum was 6.7 mg/kg in Haplic Cambisol (Přemyslov – Tři Kameny, grassland). Minimum content was 2.4 mg/kg in Arenic Cambisol (Pocoucov, arable soil). Ratio HA/FA was low ( $< 1$ ) that indicated low HS quality in all studied samples. Humification degree was low ( $< 20\%$ ) – see Tab. II. Statistically significant differences in humus quality between arable soils and grassland were found (Table III, Fig. 2, 3).

Absorbance in UV-VIS spectral range was very low and was closely connected with fractional composition of humus (Fig. 4, Table II.). At longer wavelength was HS absorption very similar for all samples. Soils (Arenic Cambisol, Eutric Cambisol and Leptic Cambisol) with low HA content showed lower absorbance at shorter wavelength. Colour indexes ( $Q_{465}$ ) calculated as a ratio of absorption  $A_{465}/A_{665}$  were high ( $> 4$ ) so that HS quality was low (Tab. II.).

Synchronous fluorescence scan spectra indicated HA presence by the following peaks: at 468/488, 482/502, 450/470 and 376/396 nm. Spectra were shifted to the longer wavelengths by the presence of polyaromatic moieties. FA presence was 340/360 nm measured. Shape of spectral curve was similar (Fig. 5) and all samples exhibited the presence of five main spectral peaks at  $\lambda_{\text{ex.}}/\lambda_{\text{em.}}$ : 468/488, 482/502, 450/470, 376/396, 340/360 at constant difference of  $\Delta\lambda = 20$  nm in 2D-synchronous fluorescence scan. Spectra were corrected at 845 V. Relative fluorescence intensity corresponded with HA and FA content in the samples, but some differences were found at the lower wavelengths (FA presence peaks).

I: Localities and selected soil properties

No	Locality	Cambisols Subtypes	Management	GPS		m.a.s.l. (m)	pH/H <sub>2</sub> O	pH/KCl	sand 2,00–0,05 (%)	silt 0,05–0,002 (%)	clay < 0,002 (%)
				N	EO						
1	Nové Město na Moravě	Haplic C.	arable	49° 32.837'	16° 4.895'	640	6.3	5.0	56.7	34.2	9.0
2	Pocoucov	Arenic C.	arable	49° 14.648'	15° 54.109'	466	6.0	4.6	71.0	22.4	6.6
3	Sněžné	Dystic C.	arable	49° 39.191'	16° 7.132'	705	7.0	6.2	55.6	31.0	13.4
4	Velká Skrovnice	Dystic C.	arable	50° 1.420'	16° 20.241'	470	6.4	5.6	35.3	49.2	15.4
5	Vojnův Městec	Dystic C.	arable	49° 40.326'	15° 52.535'	625	6.8	5.7	45.9	36.4	17.7
6	Vatín	Eutric C.	arable	49° 31.091'	15° 58.196'	530	5.1	4.8	50.0	40.0	9.5
7	Náměšť n/Oslavou	Haplic C.	arable	49° 12.808'	16° 9.757'	430	5.1	4.0	0.0	81.6	18.4
8	Přemyslov – Tři Kameny	Haplic C.	grassland	50° 10.900'	17° 5.250'	803	6.0	5.2	58.0	34.0	7.7
9	Vatín	Eutric C.	grassland	49° 31.091'	15° 58.196'	531	4.9	4.4	55.0	35.0	9.5
10	Ocmanice	Leptic C.	grassland	49° 13.909'	16° 7.782'	450	4.1	5.0	72.2	17.7	10.1

II: Total organic carbon content (TOC), humus fractionation and color indexes (Q4/6) in selected soils

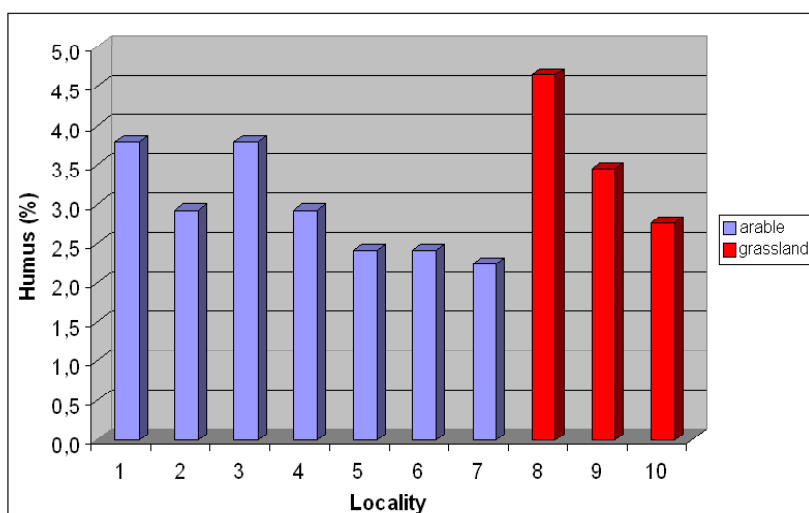
No	Locality	Cambisols Subtypes	TOC (%)	HS sum (mg/kg)	HA sum (mg/kg)	FA sum (mg/kg)	HA/FA	Humification degree (%)	Q4/6
1	Nové Město na Moravě	Haplic C.	2.2	8.9	3.9	5.0	0.8	17.7	5.9
2	Pocoucov	Arenic C.	1.7	4.0	1.5	2.4	0.6	9.0	7.6
3	Sněžné	Dystic C.	2.2	7.0	2.8	4.2	0.7	12.7	7.1
4	Velká Skrovnice	Dystic C.	1.7	6.1	2.8	3.4	0.8	16.5	6.0
5	Vojnův Městec	Dystic C.	1.4	5.0	2.0	3.0	0.7	14.3	6.7
6	Vatín	Eutric C.	1.4	7.0	3.0	4.0	0.8	21.4	7.4
7	Náměšť n/Oslavou	Haplic C.	1.3	4.7	1.6	3.0	0.5	12.6	5.7
8	Přemyslov – Tři Kameny	Haplic C.	2.7	11.0	4.3	6.7	0.6	15.9	8.0
9	Vatín	Eutric C.	1.8	8.3	2.9	5.4	0.5	16.1	8.7
10	Ocmanice	Leptic C.	1.6	4.1	1.4	2.7	0.5	9.0	9.1

## III: Analysis of variance for humus quality in different types of land use

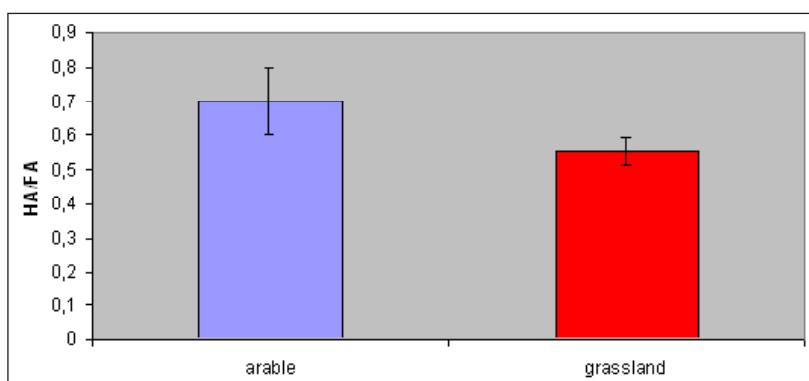
Parameter of quality	Source of variation	SS	d.f.	MS	F-ratio	P	F critical
HA/FA	Between groups	0.044	1	0.044	5.776	0.043	5.318
	Within groups	0.061	8	0.008			
	Total (corrected)	0.106	9				
Q4/6	Between groups	8.162	1	8.162	15.642	0.004	5.318
	Within groups	4.174	8	0.522			
	Total (corrected)	12.336	9				

IV: Integral areas and carbon types for  $^{13}\text{C}$  NMR spectra

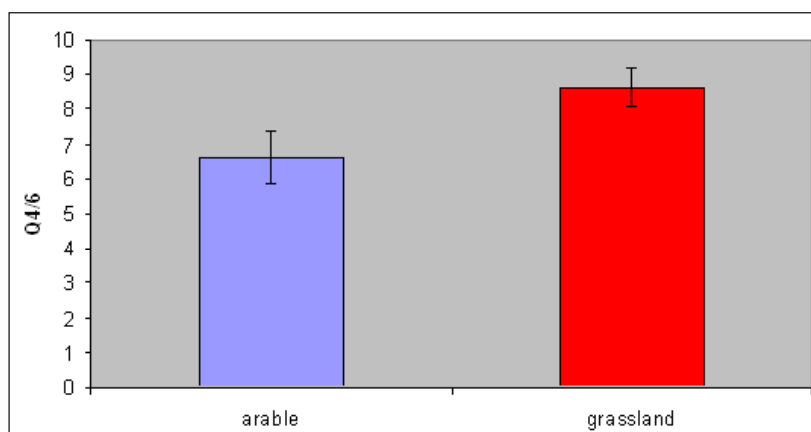
No. of areas	Spectral areas (ppm)	Types of carbon
1	230–184	carbonyl in keto and aldehyde
2	184–157	carboxyl in acids or esters
3	157–143	aromatic C-O
4	143–106	aromatic and olefinic, C-C, C-H
5	106–87	Anomers
6	87–43	sp <sup>3</sup> carbon, C-O, C-N
7	43–15	sp <sup>3</sup> carbon, C-C



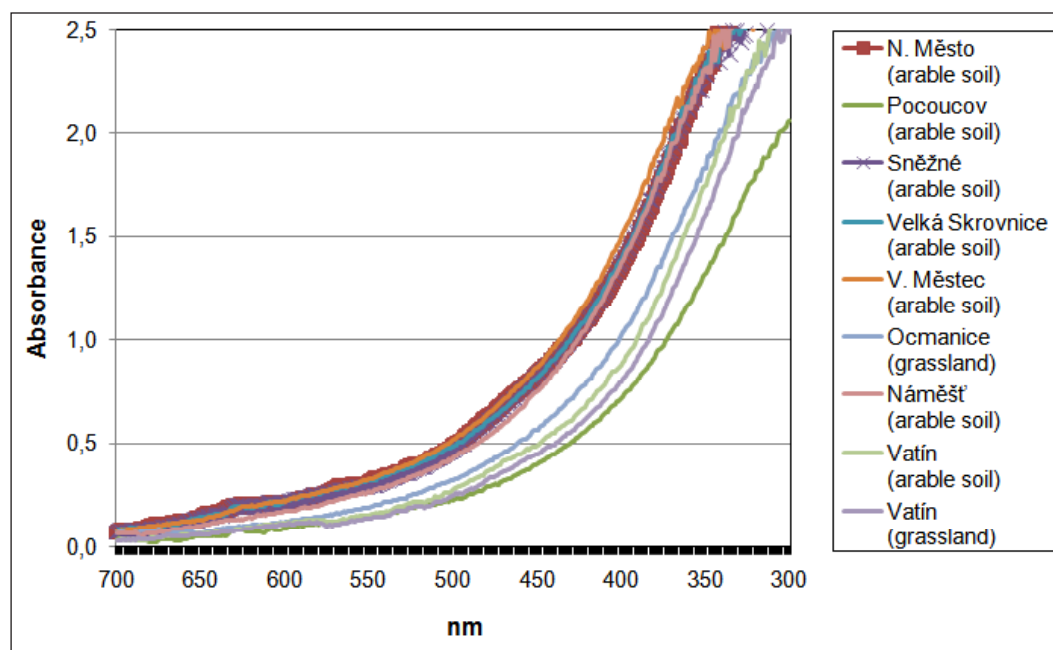
1: Humus content in selected subtypes of Cambisols



2: Humus quality under different types of land use



3: Humus quality under different types of land use

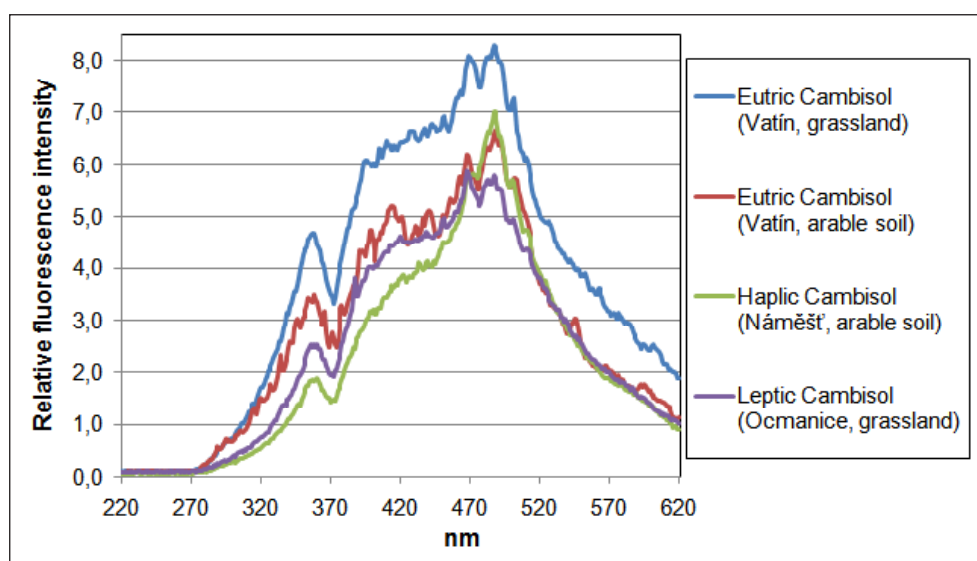


4: UV-VIS spectra in selected subtypes of Cambisols

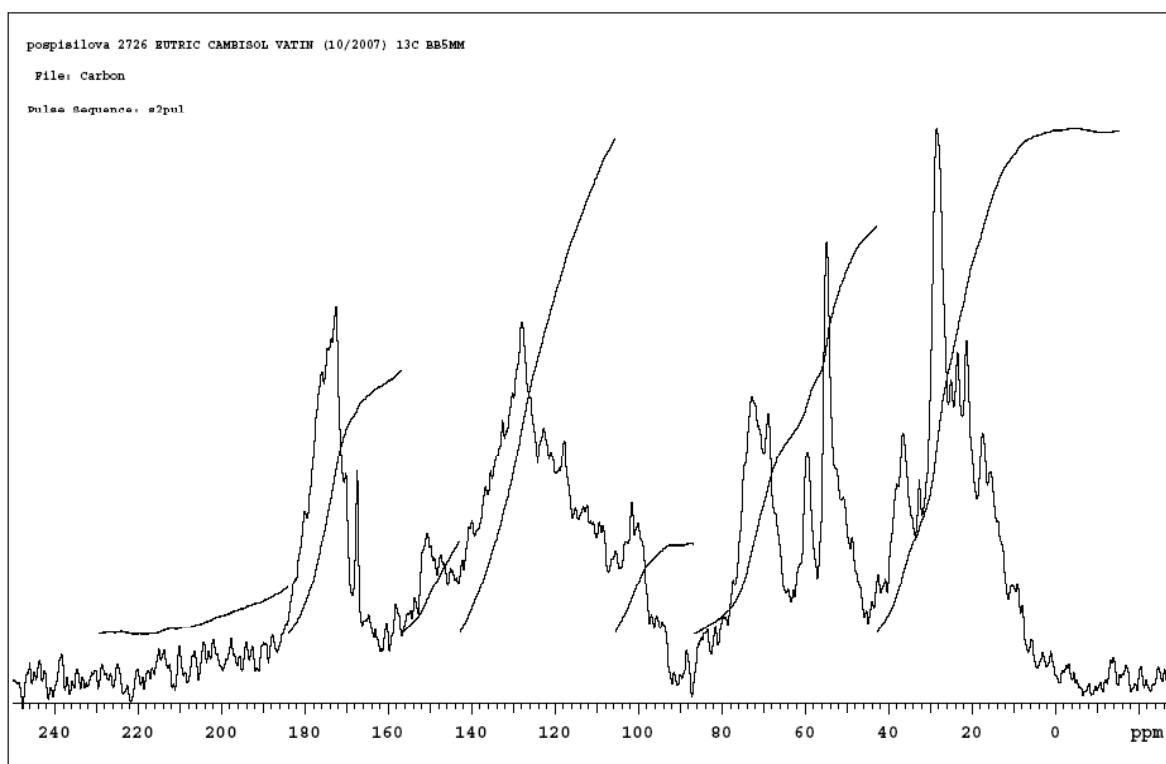
$^{13}\text{C}$ -NMR spectra in Eutric Cambisol (Vatín) are listed in Fig. 6. No differences in carbon types and content between HA isolated from grassland and arable soil were detected. Therefore the same structural composition for HA was suggested. Different groups binding in HA molecule, integral areas and carbon types in HA molecule are listed in Tab. IV. The intensity of signal detected and the spectral quality of that signal (signal: noise ratio) were dependent upon the amount of  $^{13}\text{C}$  presence in the sample and its concentration. The low amount of aromatic carbon and low spinning site peaks in Eutric Cambisol were measured. Because of low aromatic moieties ( $\text{C}_{\text{ar}}$ ) content low degree of aromaticity was determined. These findings were in agreement with UV-VIS, SFS spectroscopy. The last suggested that HA in studied soil types were young and contained more aliphatic and less aromatic compounds.

## CONCLUSIONS

Humus quality, humic acids content and quality in studied Cambisols were directly influenced by land use. Statistically significant differences in humus content and quality between arable soils and grassland were found. Cambisols widely differ in TOC content and HA content. Absorbance in UV-VIS spectral range was low and optical indexes were high. Maximum fluorescence intensity was in soils with highest humic substances content. The main fluorescence peaks for HA and FA presence were determined.  $^{13}\text{C}$  NMR spectroscopy showed that HA were young and contained more aliphatic and less aromatic components in their molecule.



5: SFS spectra of HS in grassland and arable land



6:  $^{13}\text{C}$  - NMR spectra in Eutric Cambisol (Vatín)

## SOUHRN

Celkový obsah uhlíku a kvalita humusových látek u vybraných subtypů kambizemí

Cílem naší práce bylo charakterizovat množství a kvalitu stabilních forem organického uhlíku u vybraných subtypů kambizemí pomocí nedeградаčních – spektrálních metod. Půdní vzorky byly odebrány z humusového horizontu (0–20 cm) orných půd a půd pod trvalým travním porostem (3–20 cm). Byly vybrány následující subtypy: Eutric Cambisol (lokalita Vatín – OP), Eutric Cambisol (lokalita Vatín – TTP), Haplic Cambisol (lokalita Náměšť n/Oslavou – OP), Leptic Cambisol (lokalita Ocmanice – TTP), Haplic Cambisol (lokalita Nové Město na Moravě – OP), Haplic Cambisol (lokalita Přemyslov – Tři Kameny – TTP), Arenic Cambisol (lokalita Pocoucov – OP), Dystric Cambisol (lokalita Sněžné

– OP), Dystric Cambisol (lokalita Velká Skrovnice – OP), Dystric Cambisol (lokalita Vojnův Městec – OP). Vybrané charakteristické vlastnosti různých subtypů kambizemí jsou uvedeny v Tab. I.

Celkový obsah uhlíku (TOC) byl stanoven oxidimetrickou titrací podle Nelson et Sommers (1982). Izolace HK byla provedena podle standardní mezinárodní metody IHSS (Hayes, 1985). Humusové látky (HL) byly extrahovány směsí 0,1M pyrofosforečnanu sodného a 0,1M NaOH (Podlešáková et al., 1992). Kvalita stabilních forem uhlíku představených huminovými kyselinami (HK) a fulvokyselinami (FK) byla posuzována podle absorbance v UV-VIS oblasti spektra, fluorescence (synchronních fluorescenčních spekter) a  $^{13}\text{C}$  NMR spekter. K měření spekter byly použity spektrometry Varian Cary 50 Probe s optickým vláknem, spektrofluorimetr Aminco Bowman, Series 2 a spektrometr Varian INOVA 600 (frequency 150,830 MHz).

Byl zjištěn vyšší obsah humusu a nižší kvalita humusu u půd pod trvalým travním porostem (Fig. 1, 2, 3). Maximální hodnota byla 2,7% C na lokalitě Přemyslov – Tři Kameny (TTP). Minimální hodnota byla 1,3% C na lokalitě Náměšť n/Oslavou (OP). Výsledky celkového obsahu uhlíku (TOC), frakční složení humusových látek, poměr HK/FK, stupeň humifikace a vypočítané barevné indexy ( $Q_{4/6}$ ) jsou uvedeny v Tab. II. Průměrná suma HL byla 8,4 mg/kg (TTP) a 6,4 mg/kg (OP). Maximum HL bylo zjištěno na lokalitě Tři Kameny (11 mg/kg). Minimum HL bylo u kambizemě arenické na lokalitě Pocoucov (4 mg/kg). Nejvíce HK bylo u kambizemě modální (Tři Kameny) a to 4,3 mg/kg. Nejméně HK bylo u kambizemě arenické na lokalitě Pocoucov (1,5 mg/kg). FK v průměru dosahovaly 4,7 mg/kg (TTP) a 3,7 mg/kg (OP). Maximum FK bylo opět na lokalitě Tři Kameny (6,7 mg/kg) a minimum (2,4 mg/kg) u kambizemě arenické (Pocoucov, OP). Poměr HK/FK byl nízký ( $< 1$ ) a indikoval nízkou kvalitu HL u všech vzorků. Stupeň humifikace byl nízký ( $< 20\%$ ) – viz Tab. II. Absorbance HL v UV-VIS oblasti byla nízká a korespondovala s obsahem HL (Fig. 4). Barevné indexy byly vysoké a indikovaly nízkou kvalitu HL. Vyšší fluorescence byla zjištěna u vzorků s vyšším obsahem humusových látek. Synchronní fluorescenční spektra byly podobné u všech sledovaných typů a byly ovlivněny přítomností FK (Fig. 5). U všech sledovaných vzorků bylo nalezeno pět hlavních fluorescenčních píků při  $\lambda_{\text{ex}}/\lambda_{\text{em}}$ : 468/488, 482/502, 450/470, 376/396, 340/360.

$^{13}\text{C}$ -NMR spektra byly měřeny u HK izolovaných z variant TTP a OP (Eutric Cambisol) – viz Fig. 6. Můžeme je charakterizovat jako mladé HK s vyšším podílem alifatických složek, nižším podílem aromatických složek a nízkým stupněm aromaticity.

frakční složení humusu, UV-VIS, SFS a  $^{13}\text{C}$ NMR spektroskopie, kambizemě

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