Characterisation of Soil Organic Matter in Long-term Fallow Experiment with Respect to the Soil Hydrophobicity and Wettability

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Abstract: Soil organic matter under different tillage and fertilisation systems of long-term fallow experiment established in 1958 in Prague was characterised in period of 1972–2004. This experiment consists of seven variants (control (no tillage, no manuring); farmyard manure compost (FYM); 2FYM; mineral fertilisation (NPK); 2NPK; reduced tillage (RT), and conventional tillage (CT)). In 1989, regular manuring and tillage were terminated and since then the plots have been maintained bare. Organic carbon content (C_{ox}) was analysed and the hydrophobic (A) and hydrophilic (B) functional groups were determined using Fourier-transform infrared (FTIR) spectroscopy. Hydrophobicity index (HI) and soil wettability (A/B ratio) were assessed in the experimental variants. A high significant positive correlation (r = 0.976; P < 0.05) was found, between hydrophobic functional groups (Band A) and C_{ox}, hydrophilic functional groups (Band B) did not correlate with C_{ox}. Soil wettability tended to decrease after the organic manuring was finished with the result that the values of A/B ratio were significantly different according to the farmyard manure doses applied. On the contrary, HI responded to organic manuring termination later on and no significant differences were found between different farmyard manure doses. In the variants without any fertilisation, a continual decrease in both soil wettability and hydrophobicity during the selected time period was found; the degradation process is going on in these variants.

Keywords: long-term fallow experiment; soil organic carbon; FTIR spectra; hydrophobic (A) and hydrophilic (B) functional groups; wettability; hydrophobicity

The management practices and especially the application of fertilisers and manures influence quantitatively and qualitatively soil organic matter (SOM) (Ellerbrock *et al.* 1999). A systematic study of SOM long-term changes needs (*i*) soil samples taken from plots of long-term field experiments, and (*ii*) suitable characterising tools. Non-destructive FTIR spectroscopy as one of the most sensitive infrared techniques is one of them and its application for the characterisation of organic matter and humic substances in soils is presently widely used (Ellerbrock *et al.* 2005). The FTIR spectra of humic macromolecules contain a variety of bands that are diagnostic and could serve as a valuable tool to characterise the principal classes of chemical groups of which SOM is comprised (Davis *et al.* 1999; Solomon *et al.* 2005). Besides the analyses of extracted humic substances, FTIR technique can be directly used for the study of bulk soil samples. Aliphatic C-H infrared bands in the 3000–2800 cm^{-1} region of the whole soil IR absorbance spectra can be evaluated and hydrophobicity index (HI) of the soil can be defined (Capriel *et al.* 1995). Soil organic matter

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is composed of hydrophobic carbon backbone and of functional groups which both affect soil wettability. Water repellent substances in SOM include aliphatic constituents (Capriel 1997) and waxes (Franco *et al.* 2000). The amount of hydrophilic C=O-groups (i.e. O and N containing hydroxyl and carboxyl groups) relative to that of hydrophobic CH-groups determines the hydrophobic character of SOM (Morrison & Boyd 1983). The spatial arrangement of the hydrophobic components within the soil affects water affinity that influences the resistance to microbial degradation, the rate of wetting, and the adsorption processes. These properties play an essential role in the dynamics of SOM. The aim of this study was to evaluate the long-term changes of SOM under different tillage and fertilisation systems of the long-term fallow experiment established in 1958 in Prague. Archived bulk soil samples (period 1972–2004) were spectroscopically analysed to compare their hydrophobic and hydrophilic components and to evaluate soil hydrophobicity and wettability over time. In addition, organic carbon content of the soil samples was observed to evaluate the long-term effect of the soil management on the organic carbon status.

MATERIAL AND METHODS

Soil samples. Bare fallow experiment founded on Luvi-haplic Chernozem in Prague-Ruzyně (altitude 340 m, average temperature 7.9°C, average rainfall 472 mm, pH_{KCl} 7.0) in 1958 was used as a source of soil samples. It consists of seven small plots 1.5 × 2 m with the following treatments: I – control (no tillage, no fertilisation); II – manured with farmyard manure compost (80 t/ha), tilled up to the depth of 100 mm (FYM); III – manured with farmyard manure compost (160 t/ha), tilled up to the depth of 200 mm (2FYM); IV – fertilised with mineral fertilisers in the equivalent NPK doses as in II, tilled up to the depth of 100 mm (NPK); V – fertilised with mineral fertilisers in the equivalent NPK doses as in III, tilled up to the depth of 200 mm (2NPK); VI – no manure, no mineral fertilisers, tilled up to the depth of 100 mm (RT – reduced tillage); VII – no manure, no mineral fertilisers, tilled up to the depth of 200 mm (CT – conventional tillage). In 1989, regular manuring and tillage were terminated and since then the plots have been maintained bare. Available archived soil samples (taken from 0–200 mm soil layer in the springs of 1972, 1977, 1982, 1988, 1994, 1999, 2004) were used for analyses.

Analyses. The soil samples were sieved through 2 mm sieve, air-dried and ground. For FTIR analysis, the sample (300 mg) was mixed with 900 mg KBr (FTIR grade 99%, Aldrich, Germany) and ground in an agate mortar. The homogenous mixture was transferred into a diffuse reflectance cup (dia 12 mm) without any pressure and levelled with a microscope glass slide. The FTIR spectra were measured on Thermo Nicolet Avatar 320 FTIR spectrometer equipped by Smart Diffuse Reflectance accessory. Three FTIR spectra (absorption mode, KBr background, 256 scans, data spacing 1.929 cm^{-1}) were collected with each soil sample. The FTIR spectra were analysed at two absorption bands that indicate the hydrophobic (CH-groups) and hydrophilic (CO-groups) functional groups. C-H bands (occurred at 3000–2800 cm^{-1} signal area) were denoted as absorption Band A. C-O bands (occurred at 1740–1600 cm^{-1} signal area) were denoted as absorption Band B according to Ellerbrock *et al.* (2005). The heights of the absorption Bands A and Bands B in the FTIR spectra were integrated by the spectrometer software (Omnic, version 6a) and A/B ratio was calculated.

Oxidisable carbon (C_{ox}) was determined in air dried soil samples by wet combustion according to Alten *et al.* (1935).

Hydrophobicity index (HI) was defined as the area of the aliphatic C-H infrared bands in the 3000–2800 cm^{-1} region divided by C_{ox} (Capriel *et al.* 1995).

The data were processed by analysis of variance followed by the Tukey test that evaluates the significance of differences between the variants. Correlations of the main characteristics were calculated.

RESULTS

Organic carbon content

C_{ox} of the soil samples taken from seven individual plots during the period of 1972–2004 is

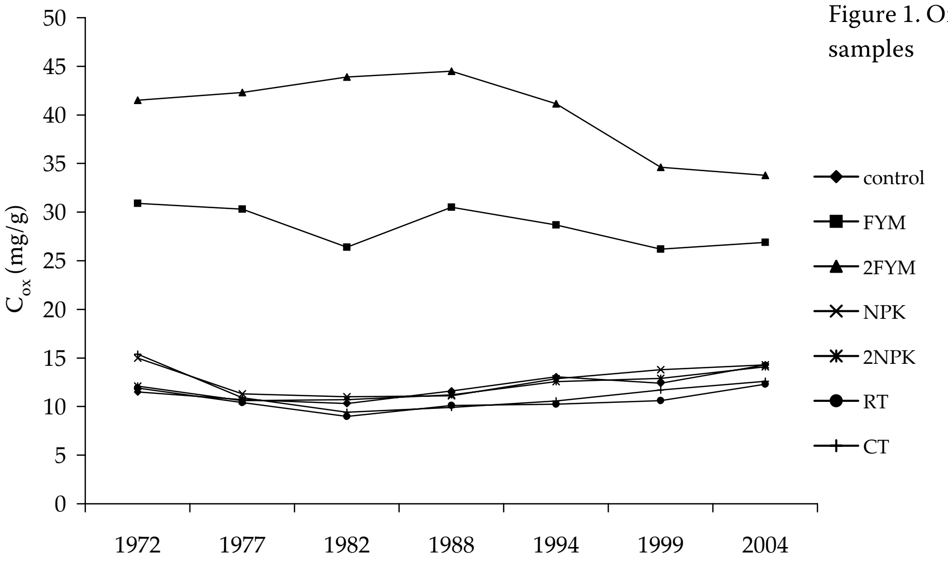

Figure 1. Organic carbon content of soil samples

shown in Figure 1. The continual application of high doses of farmyard manure compost (FYM, 2FYM plots) increased the soil organic carbon content significantly in the period of 1958–1988 as compared to the other plots (Table 1). Termination of manuring in 1989 caused a successive decrease of organic carbon content in the period 1989 till 1999, especially in 2FYM plot (by 24%). In the last period of 1999–2004, a slow decrease (2FYM) or even termination of the decrease (FYM) were observed. C_{ox} in all variants where no organic manure was applied tended to increase in the period of 1982–2004, non-significant differences having been found between them for the whole period of observation (Table 1).

FTIR spectra

Despite the fact that FTIR spectra of bulk soil samples show relatively small intensities in Bands A and B as compared to the relatively large intensities of mineral components, they can be well distinguished with spectrometer software. The highest intensities of Band A characterising hydrophobic functional groups were found for 2FYM plot followed by FYM plot (Figure 2). Significant differences were found between these two plots (Table 1). The termination of manuring in 1989 caused a successive decrease of Band A intensity in the soil samples by more than 30% in 2004 as compared to 1988 in both FYM plots. Mineral

Table 1. Average values of characterised parameters (period 1972–2004)

Variant	C_{ox} (mg/g)	Hydrophobic (A) functional groups	Hydrophilic (B) functional groups	A/B ratio	HI
Control	12.0 a[a]	0.407 a	7.839 b	0.053 a	0.035 ab
FYM	28.6 b	2.529 b	7.936 b	0.320 b	0.088 c
2FYM	40.2 c	3.542 c	8.156 b	0.436 c	0.088 c
NPK	12.8 a	0.581 a	6.941 a	0.084 a	0.047 b
2NPK	12.0 a	0.427 a	6.882 a	0.062 a	0.035 ab
RT	10.6 a	0.214 a	7.528 ab	0.029 a	0.021 a
CT	11.5 a	0.232 a	7.488 ab	0.031 a	0.020 a

[a]means within the column marked with the same letter do not differ significantly as determined by Tukey multiple range test ($P < 0.05$)

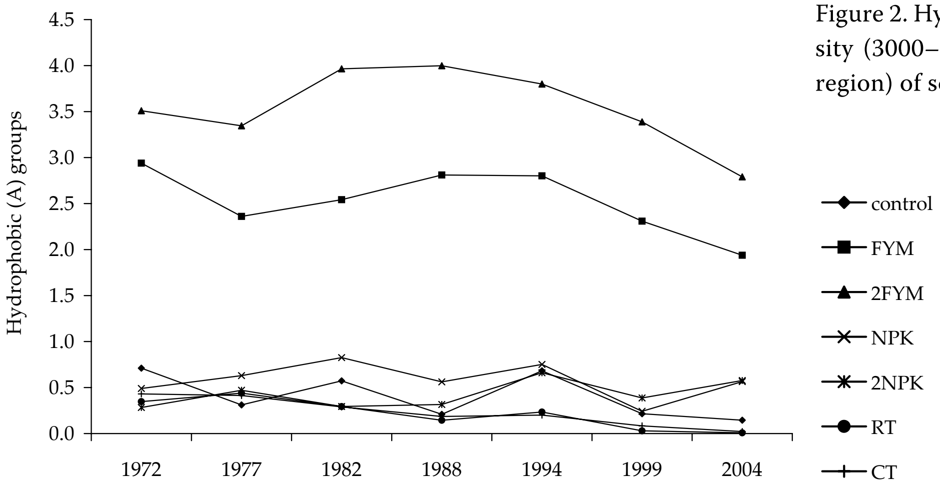

Figure 2. Hydrophobic (A) groups intensity (3000–2800 cm^{-1} absorption band region) of soil samples

fertilisation (NPK, 2NPK plots) slightly (non-significantly) increased the intensities of Band A in comparison to the unfertilised plots over the whole period of observation (Figure 2). An intensive decline of Band A intensities was found in the period of 1994–2004 in both reduced and conventional tillage (RT, CT) plots. The intensities of Band B characterising hydrophilic functional groups showed the opposite trend in both FYM plots (Figure 3). Band B in these two plots was determined as more intensive starting in 1989, when organic manuring was stopped. The intensities of Band B in the other plots varied within the range of 6.5 to 8.9 with an obvious increase in the period of 1994–2004. Significant differences between the intensities of Band B were found with FYM plots and mineral fertilised plots (Table 1).

HI and A/B ratio

Hydrophobicity index (HI) combining the data derived from FTIR spectroscopy with the data obtained from the analyses of organic carbon content was calculated (Figure 5). While both FYM plots varied within the range of 0.072 to 0.095, non-significant differences having been found for them (Table 1), the other plots oscillated at a significantly lower level (average 0.030). Only NPK plot reached higher values. According to the HI data, hydrophobicity of the soil samples taken from the farmyard compost manured plots was found as high and similar with both FYM and 2FYM plots. In 1994, soil hydrophobicity started to decline with FYM plot and, similarly, the decline appeared in 1999 with 2FYM plot. A/B ratio (CH-/CO- group ratio) reflects the chemical prop-

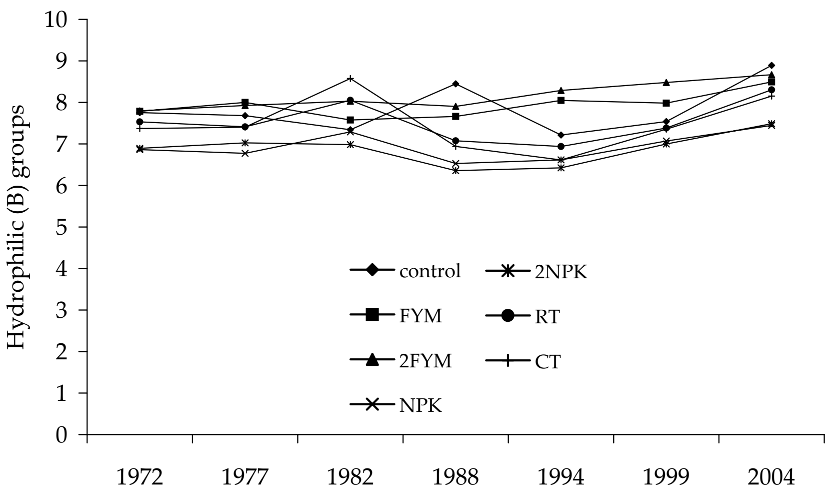

Figure 3. Hydrophilic (B) groups intensity (1740–1600 cm^{-1} absorption band region) of soil samples

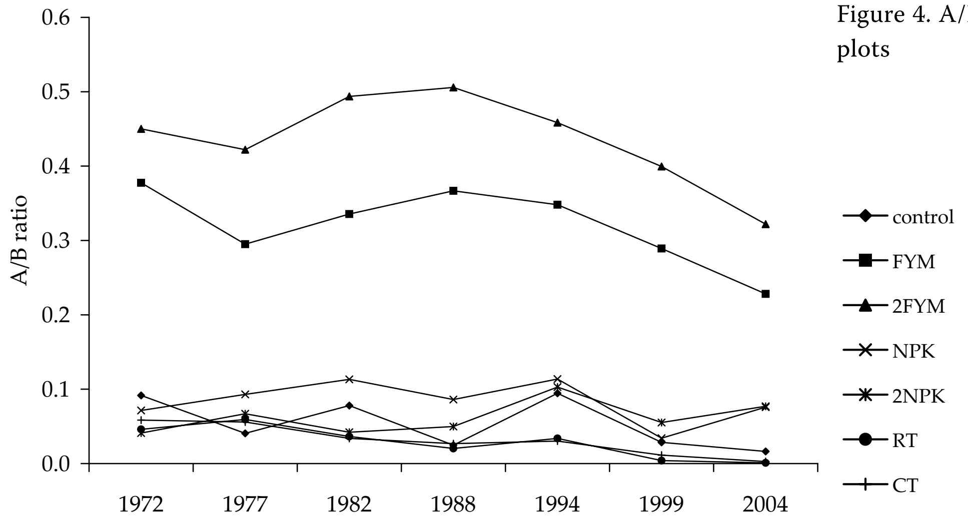

Figure 4. A/B ratio in seven individual plots

erties of soil organic matter with respect to wettability (Ellerbrock *et al.* 2005) and is calculated from the same FTIR spectra with each soil sample. A/B ratio values in the soil samples studied are given in Figure 4. The highest A/B ratio values were found in 2FYM plot; significantly lower values were calculated in FYM plot (Table 1). The both FYM plots reached significantly higher A/B ratio values as compared to the other plots. Similarly as with the intensity of Band A itself, the termination of manuring in 1989 caused a successive decrease of A/B ratio values in soil samples by more than 45% in 2004 as compared to 1988 in both FYM plots (Figure 4). No significant differences were recorded between NPK fertilised plots and control plot (Table 1). A/B ratio values for conventionally and restrictedly tilled plots without any fertilisation tended to decrease intensively in the period of 1994–2004.

Parameters relations

A high significant positive correlation ($r = 0.976$; $P < 0.05$) between hydrophobic functional groups (Band A) and C_{ox} was observed using all data measured for the calculation (Figure 6). Similar correlations were received with the data from other field experiment (Šimon 2005). On the other hand, hydrophilic functional groups (Band B) did not correlate with organic carbon content (Figure 7). Hydrophilic functional groups of SOM were affected neither by organic manuring nor by mineral fertilisation, and, on the contrary, the termination of any manipulation with soil in 1989

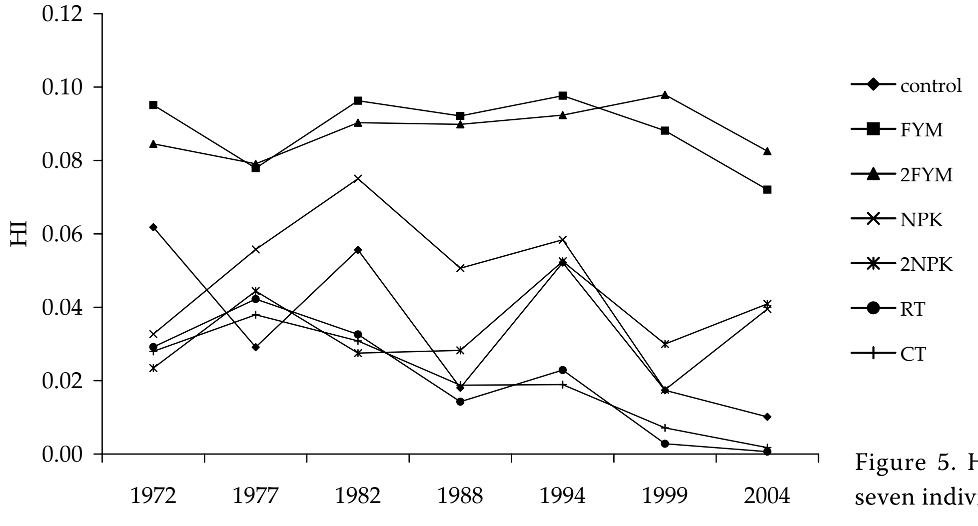

Figure 5. Hydrophobicity index in seven individual plots

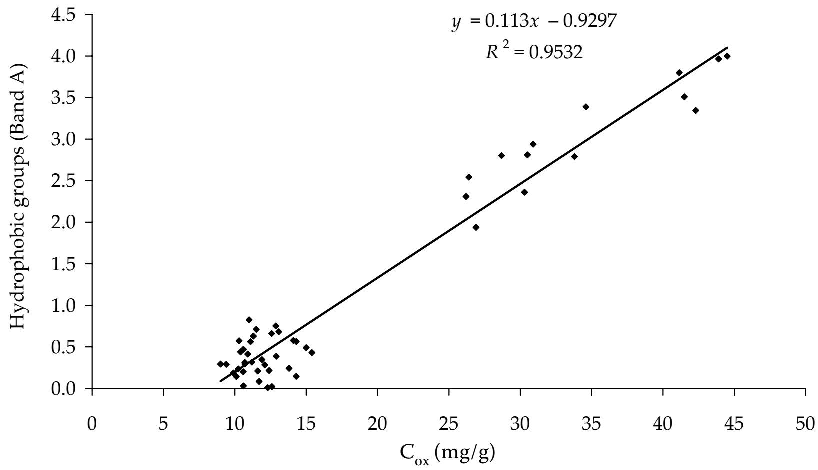

Figure 6. Hydrophobic (A) groups related to organic carbon content

supported the gradual increase of the intensity of hydrophilic components in FTIR spectra (Figure 7). Ellerbrock *et al.* (2005) found with forest bulk soil samples that A/B ratio did not correlate with soil organic carbon content. In our experiment, the A/B ratio significantly correlated with C_{ox} (Figure 8). Despite this fact, the course of the values of C_{ox} and A/B ratio differed with both parameters especially in the last period 1999–2004. While the organic carbon content increased in this period in all of the soil samples evaluated, the A/B ratio still decreased especially in FYM plots and the plots without any fertilisation. Hydrophobicity index was found to correlate significantly with the A/B ratio (Figure 9).

DISCUSSION

The studies on soil organic matter from the same soil type under different organic or mineral manuring combined with different tillage allow the determination of the effect of such practices on SOM quantity and quality. The quantity of soil organic matter is enhanced especially by the incorporation of plant residues in soil that increases their decomposition and organic matter transformation (Paustian *et al.* 1997), or by long-term application of farmyard manure that improves the nutrient status of the soil and increases organic C levels (Kubát *et al.* 1999). The quality of soil organic matter is characterised to a large extent by its stability, and SOM stability affects soil hydrophobicity (Capriel 1977) and soil wettability (Ellerbrock *et al.* 2005). In our study, the relations between soil organic carbon content and soil hydrophobicity and soil wettability were analysed for seven differently fertilised and tilled soils originated from a long-term bare fallow experiment over a period of 32 years. Our results have demonstrated that the quantity of soil

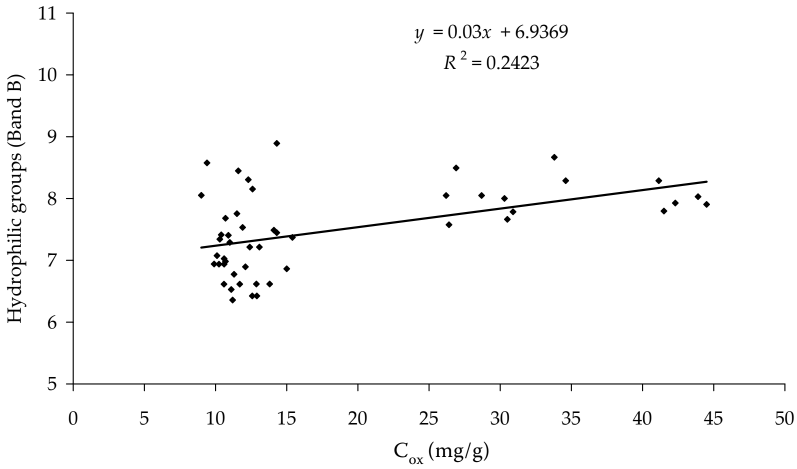

Figure 7. Hydrophilic (B) groups related to organic carbon content

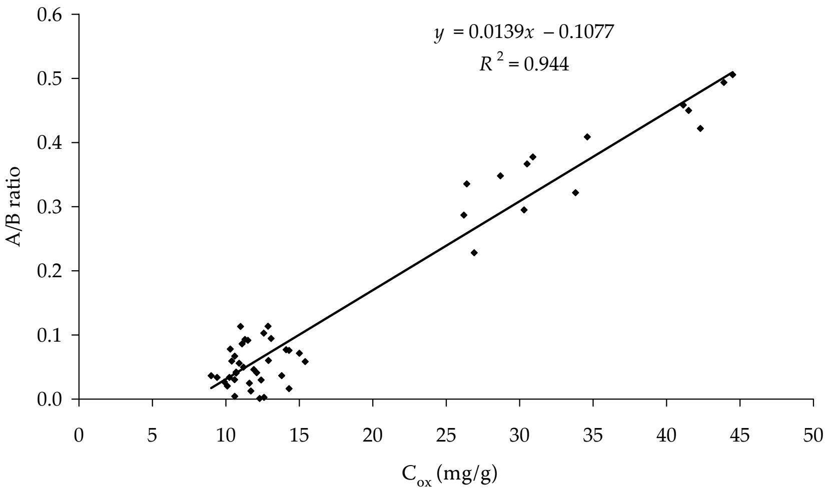

Figure 8. A/B ratio related to organic carbon content

organic C increased together with a long-term continual application of farmyard manure compost. The decomposition of the accumulated organic matter occurred later on, when no manuring was applied. Kubát and Lipavský (2006) calculated the approximate time in which the C content should reach the equilibrium value for these same two FYM plots. The calculated dates are 2019 and 2022 for FYM plot and 2FYM plot, respectively. Since 1982, the quantity of C_{ox} in plots without organic manuring has tended to be constant or to increase slightly regardless of the termination of the soil fertilisation and soil manipulation. The quality of SOM was evaluated by examining the intensities of hydrophobic (Band A) and hydrophilic (Band B) functional groups in FTIR spectra, and A/B ratio was determined as an indicator of wettability. In addition, soil hydrophobicity was assessed through the hydrophobicity index. Our results have shown that soil wettability tended to decrease after the organic manurining was finished, although the values of A/B ratio significantly differed according to the farmyard manure doses applied. Solomon *et al.* (2005) observed the accumulation of some aliphatic structures in humic substances during the composition of organic matter and a decrease of aliphatic chains following the decomposition of organic matter. On the contrary, HI responded to organic manuring termination later on and no significant differences were found with different farmyard manure doses. The variants without any fertilisation tended to decrease continually both soil wettability and hydrophobicity during the selected time period, indicating that the degradation process is going on in these variants. Solomon *et al.* (2005) found that aromatic structures are

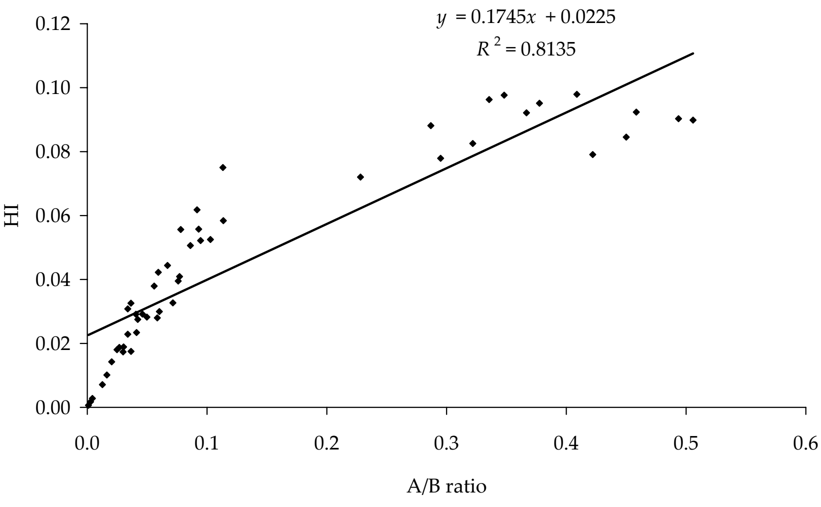

Figure 9. Hydrophobicity index related to A/B ratio

more recalcitrant and these forms are becoming the dominant forms of organic C functional groups in the humic substances extracted from the plantations and cultivated soils following land-use changes. Ellerbrock *et al.* (2005) reported that the composition of SOM was independent of the soil organic carbon content. Our results have demonstrated that while SOM quantity (i.e. organic carbon content) increased or was stabilised, SOM quality (i.e. hydrophobicity and wettability) was decreased especially in plots where no fertilisation was applied over the whole period or in plots where organic manuring had been terminated.

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