Influence of Cultivation Method on the Structure of Soil Humic Acids Estimated on the Basis of UV–VIS Absorption Spectra

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It is commonly known that a permanent crop monoculture leads to decreasing yields. One possible cause may be sought in the changes which take place in the structure and properties of humic substances. The reduced diversity of incoming substrates in a monoculture decreases the microfloral diversity. Therefore, a higher specific reactivity should be expected from the products of the humification taking place in monoculture soil. This higher specific reactivity should be found in the peripheral part of humic acid /HA/, macromolecules, particularly in those of labile HAs, less strongly associated with the mineral components of the soil.

Work was aimed at assessing the effects of the cultivation system on the structure of the humic substances produced. The assessment was based on the changes brought about by altered pH, illumination and oxidation, in the HA absorption spectra.

Materials and methods

HA preparations from soils sampled in a permanent /18 yrs/ rye monoculture and a Norfolk crop rotation during the 1986/1987 and 1987/1988 growing seasons were examined.

The soil samples were subjected to extraction according to BORATYNSKI and WILK /1965/. Labile HAs /extraction with 0.1 M $Na_4P_2O_7$ at pH 7.0/ and HAs strongly associated with mineral soil components /extraction with 0.1 M NaOH/ were obtained.

The HA absorbance in 0.005% or 0.015% carbon solutions was measured in a Varian spectrophotometer Type 635 /Techtron/ at 7 pre-selected wavelengths /294, 333, 357, 400, 416, 500 and 600 nm/.

The change in absorbance brought about by the physical and chemical factors tested was determined relative to the absorbance of HA solutions at pH 10.

The effects of the following changes were tested:

1. Change in pH within the 10.0 to 6.0 range

$$\left(\frac{\Delta A}{A}\right)_{pH} = \frac{A_{pH=10} - A_{pH=6}}{A_{pH=10}}$$

2. Illumination with visible light E = 750±50 , for one hour:

$$\left(\frac{\Delta A}{A}\right)_{h\nu} = \frac{A_{without\ h\nu} - A_{h\nu}}{A_{without\ h\nu}}$$

3. Oxidation with 0.16 M H_2O_2, the measurements being taken after 1 h:

$$\left(\frac{\Delta A}{A}\right)_{H_2O_2} = \frac{A_{without\ H_2O_2} - A_{H_2O_2}}{A_{without\ H_2O_2}}$$

Results and discussion

The relative changes in HA /$Na_4P_2O_7$/ absorbance brought about by illumination within the entire wavelength range tested are presented in Fig. 1. The HA samples from the monoculture generally showed a stronger reaction to illumination than did the crop rotation HAs.

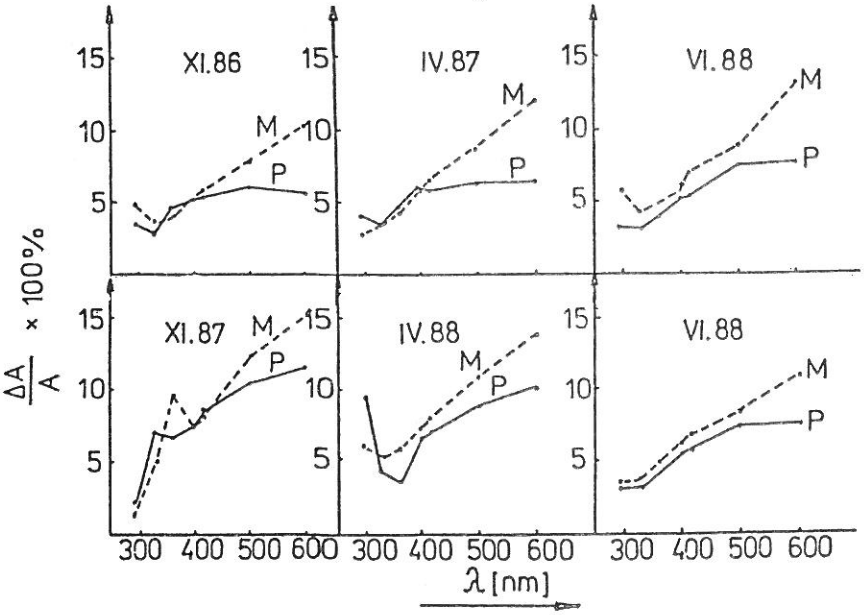

Fig. 1

The relative changes in HA /$Na_4P_2O_7$/ absorbance, brought about by illumination 1h with E = 750 μE· m^{-2}· s^{-1}. M = monoculture; P = Norfolk crop rotation

Table 1

Humic acids extracted with $Na_4P_2O_7$ and NaOH

Sampling period	Cultivation type	Extracted with $Na_4P_2O_7$						Extracted with NaOH					
		$(\frac{\Delta A}{A})$ pH		$(\frac{\Delta A}{A})$ H_2O_2		$(\frac{\Delta A}{A})$ hν		$(\frac{\Delta A}{A})$ pH		$(\frac{\Delta A}{A})$ H_2O_2		$(\frac{\Delta A}{A})$ hν	
		400 nm	600 nm	400 nm	600 nm	400 nm	600 nm x/	400 nm	600 nm	400 nm	600 nm	400 nm	600 nm x/
Nov.1986	M	13.7	16.3	8.5	15.2	5.1	10.1	13.7	20.8	9.0	13.8	6.9	8.9
	P	14.6	25.4	8.8	16.2	5.3	5.6	12.6	15.4	10.1	15.3	6.3	6.8
Apr.1987	M	13.7	22.2	9.0	17.1	6.0	11.9	11.7	17.8	10.2	15.2	7.8	15.6
	P	13.1	20.3	9.4	17.2	6.0	6.3	14.1	18.4	11.1	17.2	4.0	10.3
Jun.1987	M	12.2	24.6	9.9	17.6	5.7	13.0	13.2	19.4	11.1	16.9	8.2	15.9
	P	13.9	23.1	9.2	16.0	5.1	7.5	13.3	15.7	12.0	17.7	6.6	8.3
Nov.1987	M	13.4	23.6	8.7	18.8	7.4	14.9	11.0	18.2	8.9	14.0	6.8	14.4
	P	14.3	26.4	5.2	16.3	7.6	13.1	13.3	19.4	11.9	15.7	7.4	12.2
Apr.1988	M	14.6	26.1	11.2	19.6	7.2	13.9	15.4	20.2	11.2	17.9	7.7	9.7
	P	14.1	26.3	7.3	16.5	6.5	10.2	16.2	22.8	9.7	15.5	9.3	12.5
Jun.1988	M	14.3	24.8	10.7	19.6	5.4	10.4	15.8	21.4	11.3	17.2	7.1	11.1
	P	13.2	23.5	9.6	16.4	5.4	7.4	13.4	20.5	9.7	14.7	7.9	11.9
Average for two seasons	M	13.7	22.9	9.7	18.0	6.1	12.4	13.5	19.6	10.3	15.8	7.4	12.6
	P	13.9	24.1	8.3	16.4	6.0	8.35	13.8	18.7	10.8	16.0	6.9	10.3

M = monoculture; P = Norfolk crop rotation; x/ wavelength

The relative changes produced in HA solution absorbances by changed pH values, illumination and oxidation, measured at 400 and 600 nm, are summarized in Table 1 for HAs extracted with $Na_4P_2O_7$ and NaOH, respectively. The longwave /600 nm/ absorbance is subject to the highest relative variation produced by each factor tested.

The pH was found to exert the strongest influence on the relative absorption changes, the changes amounting to an average of 23.5% and 19.1% in labile HAs and NaOH-extracted HAs, respectively. A lower pH was observed to considerably reduce the absorbance. The reduction may be related to both the reversal of phenol group dissociation and the decreased "molecular" HA concentration produced by acidification and/or the presence of an effect similar to the hypochromic one observed in protein absorption spectra /CHANDRA and APPEL, 1978/.

The effect of oxidation on the relative changes in absorbance is lower, the changes amounting to an average of 17.2% and 16.0% in labile HAs and NaOH-extracted HAs, respectively.

Illumination exerts the weakest effect on changes in $\Delta A/A$, the changes amounting to an average of 11.5% and 10.4% for labile HAs and NaOH-extracted HAs, respectively. It is interesting to note that illumination is more effective than other factors in differentiating relative changes in the absorbance of HAs from soils in different cultivation systems.

Conclusions

The strongest relative changes in absorbance, caused by changed pH, illumination and oxidation take place in the longwave part of the spectrum.

pH causes the strongest changes.

$Na_4P_2O_7$-extracted HAs show a higher specific reactivity to the physical and chemical factors tested than do NaOH-extracted HAs.

Monoculture HAs, particularly the labile acids, show a higher specific reactivity in oxidation and photodegradation reactions than do crop rotation HAs.

References

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