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Structural characteristics and amphiphilic properties of humic acids extracted from peat soil with different reagents

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Humic acids (HAs) as the major constituents of soil organic matter actively participate in the global C cycle, influence the atmospheric CO^2 concentration and consequently, the global climate, control the fate of different contaminants in the environment. HAs are heterogeneous macromolecules with various chemical structure, size and properties. The investigation of humic fractions with different physicochemical characteristics and stability seems to be of interest, especially for peat soils in connection with the problem of their degradation.

The aim of this study was elucidation of the structural differences between humic fractions isolated from peat soil with reagents of different nature, as well as variability in their amphiphilic (hydrophobic and hydrophilic) properties.

HAs were extracted from a peat soil formed on a reed peat with the following reagents: 0.1 M NaOH, 0.1 M $Na_4P_2O_7$at pH 7, 0.1 M NaOH after extraction with 0.1 M $Na_4P_2O_7$at pH 7 and 0.1 M $NaHCO_3$.

The chemical structure and molecular parameters of HAs and their amphiphilic fractions were studied using wet-chemical, UV-VIS, IR, ^{13}C NMR-spectroscopy and gel-chromatography. Hydrophobic and hydrophilic properties of HAs were investigated with the application of hydrophobic interaction chromatography (HIC) using hydrophobic gel Octyl-Sepharose 4 Fast Flow (Pharmacia, Sweden).

Reagents of different chemical nature extracted from the peat soil HAs with different chemical structure. The HA isolated with 0.1 M $Na_4P_2O_7$at pH 7 was characterized by the highest proportion of aromatic and carboxylic C, the lowest content of both alkyl and hetero-alkyl C, the most developed systems of poly-conjugation, relatively low molecular weight, and presented the most chemically mature fraction of peat soil HA. The HA extracted with 0.1 M NaOH after pyrophosphate extraction contained less amounts of aromatic and carboxylic C and more proportions of both alkyl and hetero-alkyl C, as well as less developed systems of poly-conjugation and consecutively was a less mature HA fraction comparing with the HA extracted with sodium pyrophosphate at pH 7.

The HA isolated with 0.1 M $NaHCO_3$ was characterized by the lowest molecular weight, the lowest content of aromatic C and the highest proportions of carboxylic and hetero-alkyl C, especially carbohydrate C, as well as the least dimensions of the poly-conjugation systems in their molecules. It can be regarded as a labile fraction of peat soil HA. The HA isolated with 0.1 M NaOH without pyrophosphate extraction was the most representative peat soil HA containing humic molecules of various molecular weight and chemical structure.

Using HIC, all the HAs were fractionated on 5 fractions with different hydrophobic and hydrophilic properties excepting the labile HA extracted with 0.1 M $NaHCO_3$, which consisted only of 3 amphiphilic fractions excluding two the most hydrophobic ones. The content of the most hydrophilic components in the labile HA was near 60%.

The most chemically mature peat soil HA extracted with 0.1 M $Na_4P_2O_7$ at pH 7 contained 45% of hydrophilic components and 8% of the most hydrophobic compounds. For the less chemically mature peat soil HA extracted with 0.1 M NaOH after pyrophosphate extraction, the content of hydrophilic components was 2 times lower (23%) and the proportion of the hydrophobic ones more than 2 times higher (18%). The percentages of the chromatographic fractions for the HA isolated with 0.1 M NaOH without pyrophosphate extraction were found to be the mean values between those for both former HAs.

The most hydrophilic components of peat HAs obtained by the HIC fractionation were characterized by the largest dimensions of aromatic poly-conjugation systems, the highest content of carboxyl groups and the lowest proportion of saturated hydrocarbon

chains and polypeptides. The most hydrophobic fractions of peat HAs contained the largest amount of hydrocarbon chains and the least percentage of carboxyl groups.