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Fluorescence spectroscopy of fulvic acids from fen peatlands

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Intensive cultivation and agricultural use of peatlands lead to the degradation and mineralization of peat. Fulvic acids (FA) as the most mobile part of peat organic matter can be considered as an early indicator of its changes. One of the most sensitive and simple methods for studying the structural chemistry of humic substances is fluorescence spectroscopy. The objective of this study was to analyze comparatively the fluorescence properties of FA from low-moor peats of different genesis and decomposition degree with respect to the peculiarities of their chemical structure.

FA were isolated from 4 peat samples collected from different fen peatlands of Belarus. Fluorescence spectra were obtained on water solutions of FA at a concentration of 50 mg/L after adjustment to pH=2, 6 and 13 on a MSL-4800 spectrofluorimeter (Perkin Elmer, USA.) at 20 ± 2 ^{o}C. Emission spectra were obtained using an excitation wavelength of 365 nm. Excitation spectra were recorded by varying the excitation wavelength from 260 to 520 nm and measuring the fluorescence emission at a fixed wavelength of 520 nm. Elemental composition of FA and optical density at 465 nm (D_{465}) of FA solutions in 0.1 N NaOH were determined.

Emission spectra of FA are characterized by a broad featureless band of the maximum wavelengths at λ=460–475 nm. Excitation spectra of FA have three peaks localized in different wavelength regions. The maximum wavelengths and intensities of the excitation peaks depend on the pH values. The highest intensities are observed at pH=6. FA exhibit a main excitation peak at λ=355–370 nm, a minor peak at λ=395–400 nm, and a weak band at λ=430–440 nm. At pH=2, all the peaks decrease in intensity. With increasing the pH to 13, the excitation maximum at λ=355–370 nm shifts from 10 to 20 nm towards longer wavelengths compared to acidic solutions. A general decrease in fluorescence intensity is observed, the intensity decline of the peak at λ=355–370 nm being more marked than of the peak at 395–400 nm. These three peaks can be attributed to three types of fluorophore structures with different degrees of conjugation. The excitation peak at λ=355–370 nm is due to the phenolic units conjugated with carbonyl groups. The peak at λ=395–400 nm can be assigned to the structural components with relatively higher degrees of conjugation (various substituted bicyclic aromatic and heteroaromatic structural units). The excitation band at λ=430–460 nm is suggested to be ascribed to the aromatic polyconjugation systems, consisting of aromatic structural units connected via various bridges which do not break off the polyconjugation. The ratios of fluorescence intensities at bands 355–370 nm and 395–400 nm (I_{355}/I_{395}), 355–370 nm and 430–440 nm (I_{355}/I_{430}), as well as 395–400 nm and 430–440 nm (I_{395}/I_{430}) were calculated. These ratios may indicate to a certain extent the contributions of each type of fluorophores to the total fluorescence of the humic molecules, and, therefore, the relative contributions of the corresponding structural units to the whole molecular structure of FA.

The main fluorophores contributing to the fluorescence of FA are supposed to be phenolic units, aromatic and heteroaromatic moieties of a low degree of condensation, conjugated with functional groups and double bonds extending π-electron systems. The fluorescence properties of peat FA were found to reflect the peculiarities of their chemical structure that depend mainly on geobotanical nature of the initial peat samples. FA from reed and alder peats with the highest D_{465} and the lowest H/C ratios reflecting the most developed systems of polyconjugation in their molecules are characterized with the longest emission wavelength and the lowest ratios of I_{355}/I_{395}, I_{355}/I_{430}, and I_{395}/I_{430}. These ratios suggest the most significant contribution of the aromatic polyconjugation systems to the fluorescence of these FA. The highest I_{355}/I_{395}, I_{355}/I_{430}, and I_{395}/I_{430} ratios found for sedge-peat FA confirm that the aromatic polyconjugation systems in its molecules are less developed.