

Investigation of dissolved organic substances in the Northern Dvina under different hydrological seasons

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The rivers of the Russian Arctic, which include the Northern Dvina, are important sources of organic matter of terrestrial origin to the seas of the Arctic Ocean. The Northern Dvina River accounts for ~50% of the entire flow of the river system to the White Sea. The spring freshet period accounts for ~60% of the annual hydrological flow, and ~80% of the annual flow of riverine suspended sediment. Despite the importance of the study of organic matter in dissolved form for global carbon cycling, this topic has received little attention in this region of Russia. This paper presents results from a study examining dissolved organic matter (DOM) in the Northern Dvina River encompassing different hydrological seasons, utilizing a range of methods for isolation and concentration. The goal of this study was to characterize the molecular features of DOM in the Northern Dvina River across the seasonal hydrograph. IR spectra of the samples were recorded on a FTIR spectrometer Vertex 70 (Bruker, Germany), with a resolution of 4 cm⁻¹, measuring the range 4000-400 cm⁻¹ and 128 recorded parallel determinations. The absorption band at 3200 cm⁻¹ and 1600 cm⁻¹ are due to OH group. In the range of 2800-3000 cm⁻¹ we observed bands due to methyl, methylene groups, and possibly the presence of nitrogen-containing C = NH groups. In the area of 1710 cm⁻¹ there is a strong band of carbonyl groups characteristic of aldehydes, ketones and carboxylic acids. The mild band at 1450 cm⁻¹ is noted and can be attributed to the C-C vibrations of the aromatic ring. In the range of 1100-1000 cm⁻¹ is observed a band related to C-O groups. The absorption bands at 1030 cm⁻¹ correspond to C-O-C symmetric stretching vibrations, and at the 1150 cm⁻¹ belongs to the aromatic C-H-planar deformation fluctuations. Based on data from the infrared spectrometry, it should be noted that along with the strongly expressed aliphatic component, studied samples are characterized by the presence of aromatic ring groups. An important contribution of aliphatic groups and the presence of aromatic structures are also confirmed with solid-state NMR spectroscopy (NMR spectrometer Bruker AVANCE III™ 600). The relative intensity was normalized by the intensity of the weakest signal, the spectrum was deconvoluted to separate signals. Methods of cross-polarization ¹H-¹³C and magic angle spinning (CP/MAS) were used in order to improve the resolution (spinning rate was 12 kHz). The spectrum was registered for ¹³C, the number of scans was 2048 and the relaxation delay was 5 s. According to the GPC molecular weight distribution, DOM samples analyzed from during the autumn floods from the Northern Dvina River are 10kDA, which corresponds to the molecular masses of fulvic acids. This data is the first obtained describing structural group DOM components from the Northern Dvina River methods using IR and NMR spectroscopy. Comparative analysis of the DOM samples obtained at different hydrological seasons and using different methods of selection and concentration, highlights the predominance of aliphatic structure in comparison to the aromatic component, which indicates a high replacement hydrocarbon skeleton in the samples studied.

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